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SOME LIMITATIONS ON THE POSSIBLE COMPOSITION OF THE ORE-FORMING FLUID[1]

PAUL B. BARTON, JR.

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ABSTRACT

The activity ratios of various important anions ($S^=$, $CO_3^=$, $SO_4^=$, OH^-, F^-, and Cl^-) in hydrothermal solutions at the time of deposition are evaluated using a simple thermodynamic technique. The ratios are interpreted in the light of the mineralogy of ore deposits and limits are placed on the variability of each ratio in hydrothermal solutions. All of the calculations are made for 25° C and cautious extrapolation to higher temperatures seems justified; however, additional data for elevated temperatures and pressures are needed before more than approximate values may be assigned to these ratios in the ore-forming fluid.

The calculated partial pressure of CO_2 in the ore fluid is generally less than one atmosphere, which suggests that a dense CO_2 phase cannot be considered an important ore fluid for most deposits. The partial pressure of H_2S is usually less than 10^{-4} atmosphere, which makes it extremely difficult to defend the theory that metals (other than the easily complexible mercury, arsenic, antimony, and perhaps gold and silver) are transported in quantity as complex sulfides or hydrosulfides. The sulfate to sulfide ratio is such that the oxidation potential at the time of deposition is defined by the following equation: Eh (in volts) $= 0.22 \pm 0.04 - 0.059$ pH.

[1] Publication authorized by the Director, U. S. Geological Survey.

INTRODUCTION

THIS paper presents and discusses some of the implications of a series of simple calculations by which relative values can be placed on the activities (effective concentrations) of the various anions present in the dominantly aqueous fluids from which hydrothermal ores are presumed to be precipitated. At present the geologic and chemical data are inadequate to permit a rigorous evaluation of the anionic ratios for any real hydrothermal deposit, thus this article introduces a new approach to the problem of the ore-forming fluid rather than a final answer.

This discussion is not limited to a single deposit or type of deposit; but, in a broader sense, it may apply in principle to the whole gamut of deposits that make up the group generally classified as hydrothermal. It is not within the scope of this paper to attempt to evaluate the status of borderline or questionable types of deposits, though a truly genetic classification of ore deposits may evolve through further investigation and application of the ideas proposed here. The main contribution of this paper lies in the interpretation of mineral assemblages generally found in hydrothermal ore deposits in the light of calculations such as those illustrated below.

NATURE OF THE CALCULATIONS

With the minor exception of the native elements, the ore and gangue minerals are composed of combinations of metallic cations and various anions. In hydrothermal environments some elements, such as lead or mercury, always precipitate as sulfides (neglecting sulfosalts). Others may combine with several types of anions; for example, calcium occurs in calcite, fluorite, or anhydrite. The particular combination of anions and cations that precipitates (assuming no metastable phases) from a solution is that which is the most stable, or in other words, the least soluble (i.e., the reaction is accompanied by a greater decrease in free energy than is possible with any other reaction). The free energy changes, and consequently the activity product constants, for most of the reactions of interest are known at room temperature and pressure; therefore, the relative activities of the anions can be calculated as is shown by the example below. The thermodynamic calculations presented here are made from data taken entirely from Latimer (9) and thus are subject to any revisions or corrections that may apply to his information.

If conditions are chosen such that the crystalline sulfide and carbonate of a metal, e.g., MnS and $MnCO_3$, are in equilibrium with the same solution, then the ratio of the sulfide ion activity to carbonate ion activity may be related through the activity product constants.

$$MnS = Mn^{++} + S^{=} \qquad K_{MnS} = a_{Mn^{++}} \cdot a_{S^{=}} = 10^{-15.16}$$

$$MnCO_3 = Mn^{++} + CO_3^{=} \qquad K_{MnCO_3} = a_{Mn^{++}} \cdot a_{CO_3^{=}} = 10^{-10.06}$$

By equating:

$$\frac{10^{-15.16}}{a_{S^{=}}} = a_{Mn^{++}} = \frac{10^{-10.06}}{a_{CO_3^{=}}}; \qquad \frac{a_{S^{=}}}{a_{CO_3^{=}}} = \frac{10^{-15.16}}{10^{-10.06}} = 10^{-5.10}.$$

Therefore, when the $a_{S^=}/a_{CO_3^=}$ ratio is greater than $10^{-5.1}$ MnS will precipitate instead of $MnCO_3$; if the ratio is less than $10^{-5.1}$ the carbonate will form rather than the sulfide. It must be realized that this does not predict whether or not a precipitation will occur; it only predicts whether the product of a precipitation will be a carbonate or a sulfide.

By modifying the equations slightly it is possible to include some simple silicates. The equations are written so as to give quartz as a dissolution product of the silicates. This procedure avoids the necessity of dealing with the poorly characterized soluble forms of silica, and is geologically and chemically permissible because quartz generally is associated with the other vein minerals in hydrothermal deposits. In effect, the calculations merely define the conditions under which a given mineral is stable in association with quartz. The following are a typical set of reactions:

$$MnSiO_3 + H_2O = Mn^{++} + 2OH^- + SiO_2$$

$$K_{MnSiO_3} = a_{Mn^{++}} \cdot a^2_{OH^-} = 10^{-13.20}$$

$$Mn(OH)_2 = Mn^{++} + 2OH^-$$

$$K_{Mn(OH)_2} = a_{Mn^{++}} \cdot a^2_{OH^-} = 10^{-12.70}$$

and from the preceding paragraph, $K_{MnCO_3} = 10^{-10.06}$. There are now two $a_{CO_3^=}/a^2_{OH^-}$ ratios, the first equals $10^{3.1}$ and represents the boundary between $MnCO_3$ and $MnSiO_3$. The second ratio is $10^{2.6}$ and it defines the boundary between $MnCO_3$ and $Mn(OH)_2$. It is readily seen that if the $a_{CO_3^=}/a^2_{OH^-}$ ratio is low enough for $Mn(OH)_2$ to form instead of $MnCO_3$, the ratio is also more than low enough for $MnSiO_3$ to form. Therefore, $Mn(OH)_2$, pyrochroite, is incompatible with quartz and it should occur only in silica-deficient environments.

A method similar to that employed for the silicates is used to evaluate activity product constants for reactions involving magnetite. In this case the trivalent iron is assumed to go to hematite on the solution of the magnetite as is indicated by the following reaction: $Fe_3O_4 + H_2O = Fe_2O_3 + Fe^{++} + 2OH^-$. The application of ratios involving this reaction is somewhat limited by the fact that neither magnetite nor hematite are common hydrothermal minerals in low-temperature deposits (the data presented are insufficient to justify extrapolation to high temperatures). However, the calculations do predict whether or not magnetite and hematite are stable in the wallrock adjacent to the ore body.

The type of calculations illustrated above has been made for various combinations of geologically significant anions and metallic cations. The activity product constants have been taken from data given by Latimer (9) and are summarized in Table 1. The anionic activity ratios at the time of deposition are presented in Table 2 and are shown graphically in Figure 1.

ASSUMPTIONS AND RESTRICTIONS

These calculations of the anionic ratios apply rigorously only to the solutions from which the compounds used to evaluate the ratio are precipitated; they do not consider condition of transport. Although an ideal

TABLE 1

ACTIVITY PRODUCT CONSTANTS[a] (DATA FROM LATIMER)

Cation	$S^=$	$CO_3^=$	$SO_4^=$	$(F^-)^2$	$(Cl^-)^2$	$(OH^-)^2$	
						Hydroxide	Silicate
Fe^{++}	[b] $10^{-18.40}$	$10^{-10.68}$	s	s	s	[c] $10^{-14.76}$	[d] $10^{-18.92}$
Ni^{++}	$10^{-27.70}$	$10^{-6.87}$	s	s	s	$10^{-15.29}$	—
Co^{++}	$10^{-20.72}$	$10^{-12.10}$	s	s	s	$10^{-15.69}$	—
Pb^{++}	$10^{-28.16}$	$10^{-13.13}$	$10^{-7.89}$	$10^{-7.40}$	$10^{-4.80}$	$10^{-14.31}$	[e] $10^{-16.38}$
Sn^{++}	$10^{-26.00}$	s	s	s	s	$10^{-26.13}$	—
Zn^{++}	$10^{-24.16}$	$10^{-9.70}$	s	s	s	[f] $10^{-16.46}$	[g] $10^{-21.03}$
Cd^{++}	$10^{-26.00}$	$10^{-11.28}$	s	s	s	$10^{-13.70}$	—
Hg^{++}	$10^{-53.00}$	—	s	s	s	[h] $10^{-25.12}$	—
Ca^{++}	$10^{-2.04}$	$10^{-8.33}$	$10^{-4.44}$	$10^{-9.77}$	s	$10^{-5.09}$	[i] $10^{-11.05}$
Sr^{++}	s	$10^{-9.18}$	$10^{-6.13}$	$10^{-9.10}$	s	$10^{-3.49}$	[j] $10^{-4.91}$
Ba^{++}	s	$10^{-8.30}$	$10^{-9.93}$	$10^{-4.62}$	s	$10^{-2.30}$	s
Mn^{++}	$10^{-15.16}$	$10^{-10.04}$	s	s	s	$10^{-13.70}$	[k] $10^{-13.30}$
Cu^{++}	$10^{-36.10}$	[m] $10^{-9.60}$	s	s	s	[n] $10^{-13.90}$	—
$(Cu^+)^2$	$10^{-48.92}$	—	s	s	$10^{-13.60}$	$10^{-29.71}$	—
$(Ag^+)^2$	$10^{-50.24}$	$10^{-11.09}$	s	s	$10^{-19.10}$	[p] $10^{-15.48}$	—

[a] The least soluble phase is chosen whenever there is a choice. Compounds present as hydrothermal vein minerals are underlined. s means the compound is soluble or decomposes in water; — indicates that no data are available.

[b] For pyrite the $a_{S^=} \cdot a_{Fe^{++}} = 10^{-30.33}$.

[c] This figure is for $Fe(OH)_2$; if reactive Fe_2O_3 is present, magnetite forms with the $a^2_{OH^-} \cdot a_{Fe^{++}} = 10^{-19.43}$.

[d] This figure is for $FeSiO_3$.

[e] This figure is for Pb_2SiO_4.

[f] This figure is for ZnO, zincite, questionably hydrothermal.

[g] This figure is for $ZnSiO_3$.

[h] This figure is for HgO red.

[i] This figure is for $CaSiO_3$, wollastonite.

[j] This figure is for $SrSiO_3$.

[k] This figure is for $MnSiO_3$, rhodonite.

[m] $CuCO_3$ is only an approximation of the basic copper carbonates.

[n] This figure is for CuO.

[p] This figure is for Ag_2O.

situation exists when both compounds used to evaluate a ratio occur together as hydrothermal minerals, a good deal of information may be gained when only one member of the pair is present. For example, SrF_2 is unknown as a hydrothermal mineral, but $SrCO_3$ does occur. Therefore, using the data from Table 2, it can be concluded that the $a_{CO_3^=}/a^2_{F^-}$ ratio in the fluid from which $SrCO_3$ was being precipitated was greater than $10^{-0.1}$.

If neither of the compounds represented in the ratio is found in primary ore deposits, the ratio has little application for such deposits. For example, the $a_{CO_3^=}/a_{SO_4^=}$ ratio for lead is $10^{-4.9}$, but it has no significance for primary ores because lead is always a sulfide (or sulfosalt) there. However, this particular ratio is useful in explaining the relation of cerussite to anglesite in oxidized lead ores.

A thermodynamic treatment of solubilities such as this requires the

TABLE 2

ANIONIC ACTIVITY RATIOS IN A SOLUTION IN EQUILIBRIUM WITH SOLID PHASES OF A CATION AND EACH OF THE ANIONS APPEARING IN THE RATIO

Cation	Anionic ratios								
	$\frac{a_{S^=}}{a_{CO_3^=}}$	$\frac{a_{S^=}}{a^2_{OH^-}}$		$\frac{a_{CO_3^=}}{a^2_{OH^-}}$		$\frac{a_{CO_3^=}}{a_{SO_4^=}}$	$\frac{a_{CO_3^=}}{a^2_{F^-}}$	$\frac{a_{SO_4^=}}{a^2_{F^-}}$	$\frac{a_{S^=}}{a^2_{Cl^-}}$
		Oxide or hydroxide	Silicate	Oxide or hydroxide	Silicate				
Fe^{++}	$10^{-7.7}$	$10^{-2.7}$	$10^{+0.8}$	$10^{+4.1}$	$10^{+8.8}$	—	—	—	—
Ni^{++}	$10^{-20.6}$	$10^{-11.6}$	—	—	—	—	—	—	—
Co^{++}	$10^{-14.6}$	$10^{-11.1}$	—	—	—	—	—	—	—
Pb^{++}	$10^{-13.3}$	$10^{-13.3}$	$10^{-11.8}$	—	—	—	—	—	$10^{-23.4}$
Sn^{++}	—	$10^{+0.6}$	—	—	—	—	—	—	—
Zn^{++}	$10^{-15.5}$	$10^{-8.7}$	$10^{-4.1}$	$10^{+6.7}$	$10^{+9.8}$	—	—	—	—
Cd^{++}	$10^{-16.7}$	$10^{-14.3}$	—	—	—	—	—	—	—
Hg^{++}	—	$10^{-26.2}$	—	—	—	—	—	—	—
Ca^{++}	$10^{+5.3}$	$10^{+2.0}$	$10^{+5.1}$	$10^{-2.4}$	$10^{+2.7}$	$10^{-5.9}$	$10^{+1.4}$	$10^{+8.3}$	—
Sr^{++}	—	—	—	—	$10^{-4.39}$	$10^{-8.0}$	$10^{-0.1}$	$10^{+8.0}$	—
Ba^{++}	—	—	—	—	—	$10^{0.0}$	$10^{-4.2}$	$10^{-4.2}$	—
Mn^{++}	$10^{-5.1}$	$10^{-2.4}$	$10^{-2.0}$	$10^{+2.6}$	$10^{+5.1}$	—	—	—	—
Cu^{++}	$10^{-20.5}$	$10^{-17.3}$	—	—	—	—	—	—	—
Cu^{+}	—	$10^{-19.2}$	—	—	—	—	—	—	$10^{-35.9}$
Ag^{+}	$10^{-20.2}$	$10^{-24.9}$	—	—	—	—	—	—	$10^{-21.2}$

Other ratios of interest:

$\frac{a_{S_2^=}}{a_{CO_3^=}}$ for $FeS_2 - FeCO_3 = 10^{-19.6}$

$\frac{a_{S_2^=}}{a^2_{OH^-}}$ for $FeS_2 - Fe_3O_4 = 10^{-19.6}$

$\frac{a_{S_2^=}}{a_{S^=}}$ for $FeS_2 - FeS = 10^{-11.6}$

$\frac{a_{CO_3^=}}{a^2_{OH^-}}$ for $FeCO_3 - Fe_3O_4 = 10^{+8.7}$

$\frac{a_{S^=}}{a^2_{OH^-}}$ for $FeS - Fe_3O_4 = 10^{+1.6}$

fundamental assumption that equilibrium conditions prevail. This precludes extensive transport by such metastable phases as supersaturated solutions or colloids (though precipitation through a colloidal stage is permissible). If great departures from equilibrium are noted, the validity of these calculations is seriously questioned. On the other hand, deviations from equilibrium that might be represented by the formation of aragonite instead of calcite or marcasite instead of pyrite (assuming that aragonite and marcasite are truly metastable under the conditions of precipitation) have comparatively little effect on the anionic ratios as applied in this consideration. As is shown in Figure 1, the calculated ratios form a very well-knit pattern whose consistency is in itself an argument for approximately equilibrium conditions. There are no anomalous compounds appearing out of place in Figure 1, and the mineral associations in ore deposits are in good agreement with the hydrothermal regions shown.

These calculations are based on thermodynamic values in aqueous systems at 25° C and 1 atmosphere, but all hydrothermal deposits are believed to have originated at temperatures and pressures greater than this. There-

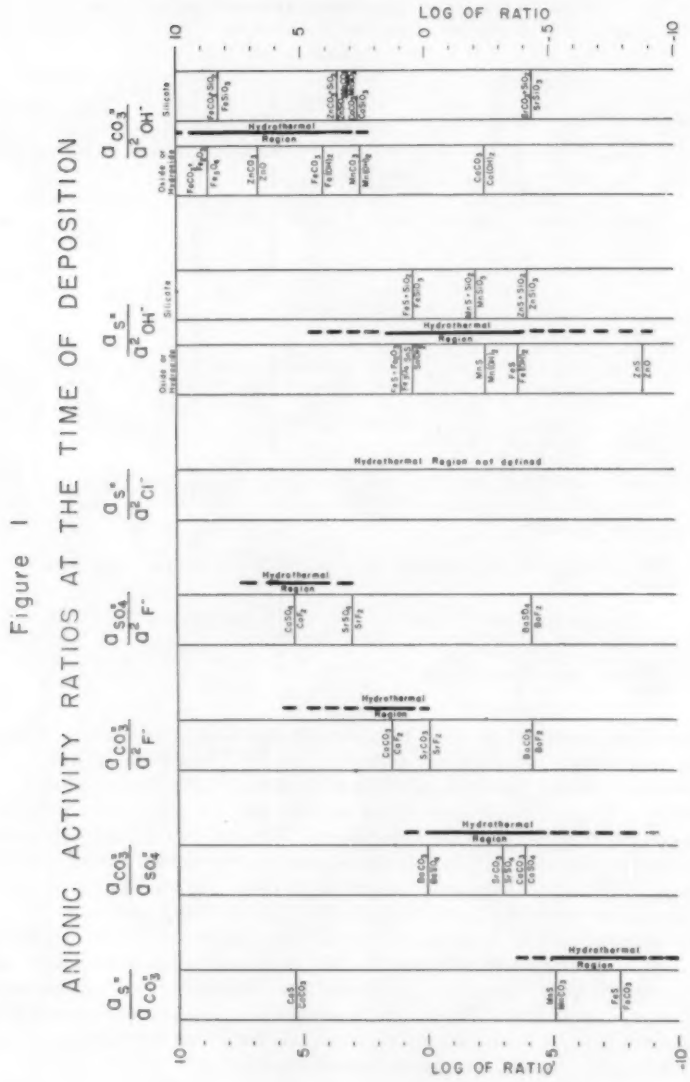
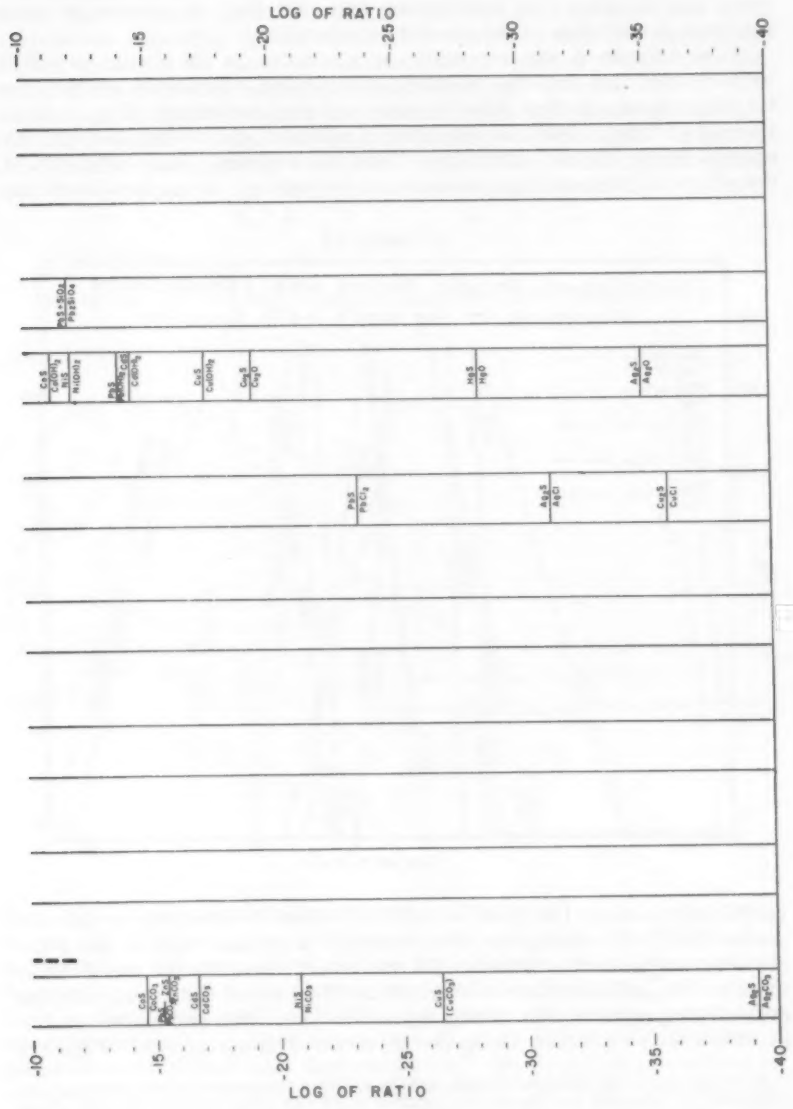


Figure 1

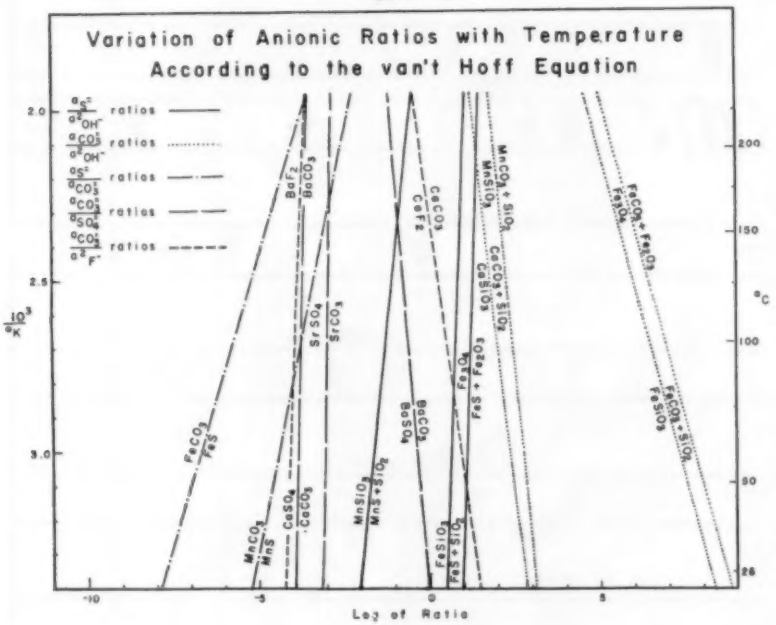
ANIONIC ACTIVITY RATIOS AT THE TIME OF DEPOSITION


LOG OF RATIO
-10
-15
-20
-25
-30
-35
-40
PbS+SO4
Pb3(PO4)2
CoS
Co(OH)2
NiS
Ni(OH)2
PbS
Pb(OH)2
CdS
Cd(OH)2
CuS
Cu(OH)2
CuS
Cu2O
HgS
HgO
Ag2S
Ag2O
PbS
PbCl2
Ag2S
AgCl
Cu2S
CuCl
CoS
CoCO3
NiS
NiCO3
CdS
CdCO3
PbS
PbCO3
NiS
NiCO3
CuS
Cu(CO3)2
Ag2S
Ag2CO3
LOG OF RATIO

fore, *these figures merely represent approximations* that become increasingly tenuous as conditions deviate more and more from standard conditions. Owen and Brinkley (10) have shown that the effect of pressure on ionic equilibria is negligible in the present consideration.

It is difficult, if not impossible, to generalize on the extent to which room-temperature data may be safely extrapolated. Inasmuch as the ratios for different metals often differ by many orders of magnitude (Fig. 1), large thermal variation of the activity product constants can be tolerated without entirely destroying the significance of the calculations. Some indication of the effects of increased temperature can be obtained by application of the

Figure 2



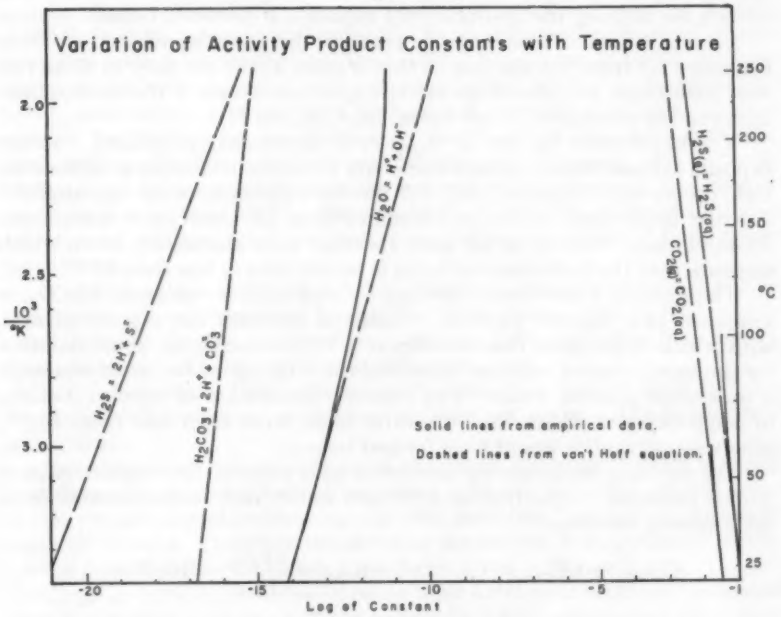
van't Hoff equation, $d \ln K/dT = \Delta H/RT^2$, where K is the activity product constant, ΔH is the change in heat content, R is the gas constant and T the absolute temperature. Because ΔH varies with temperature and because there are not sufficient data to evaluate ΔH for most of the reactions at the desired temperatures, the above expression *gives only approximate values* for the activity product constants at elevated temperatures.[2] Figure 2

[2] Calculations of the solubility of some sulfides at higher temperatures have been made by Verhoogen (15) who took into account the variation of ΔH with temperature for the solid phases but was unable to evaluate the $d\Delta H/dT$ for the soluble constituents; thus his data are subject to re-evaluation.

shows the variation in anionic-activity ratios with temperature for some of the significant metals as determined by the van't Hoff equation. Figure 3 shows the variation of a few selected activity product constants with temperature according to the van't Hoff equation, and the empirically derived constants for three of the reactions are plotted to illustrate the nature of the departure from the calculated values.

The lack of thermodynamic and chemical data has prevented the consideration of many compounds such as chalcopyrite, dolomite, sulfosalts, and most silicates. Some of the natural compounds are much more complex than the simple ones for which the thermodynamic data are available.

Figure 3



Examples of such approximations in these calculations are: SnS for stannite or teallite, $FeSiO_3$ for more complex silicates such as chlorite, $CaSiO_3$ for more complex silicates such as zeolites, amphiboles, epidotes, or pyroxenes. In these cases the complex natural compounds are necessarily more stable than are the simple ones used in the calculations, otherwise the simple ones would occur instead. This means that the ratio calculated represents a minimum or maximum value depending on whether the approximated simple compound is in the denominator or numerator of the ratio. For example, the $a_{S^-}/a^2_{OH^-}$ ratio for $FeS\text{-}Fe(OH)_2$ is $10^{-3.7}$, but because the ferrous oxide mineral is magnetite, $FeO \cdot Fe_2O_3$ or Fe_3O_4, the ratio given is only a lower

limit and the FeS-Fe_3O_4 boundary must be at a ratio greater than $10^{-3.7}$. Fortunately, in this particular reaction the "more complex compound" is magnetite for which there are thermodynamic data, and the activity product constant for the reaction $Fe_2O_3 + Fe^{++} + 2OH^- = Fe_3O_4 + H_2O$ can be calculated. This leads to $a_{S^-}/a^2_{OH^-}$ ratio of $10^{1.0}$ which is almost five orders of magnitude larger than that given by the simple compound $Fe(OH)_2$. Therefore the investigator must be especially careful when using simple compounds to represent more complex ones.

DEFINITION OF THE HYDROTHERMAL REGIONS

The ratios related to the primary ore minerals are given in Figure 1 and the regions of deposition from hydrothermal fluids are indicated. The criteria for defining the hydrothermal regions are discussed below.

$a_{S^-}/a_{CO_3^-}$ ratio.—This ratio is perhaps the most significant of those evaluated by these calculations in that it gives a clue not only to these two ions themselves, but also to the relative amounts of two of the most important volatile substances in ore fluids, i.e., CO_2 and H_2S.

The upper limit for the $a_{S^-}/a_{CO_3^-}$ ratio is not sharply defined. In ore deposits calcium always prefers carbonate to sulfide (the mineral oldhamite, CaS, occurs only in meteorites), and therefore the ratio never exceeds $10^{5.3}$. A better upper limit can be approximated from the behavior of manganese. Rhodochrosite, $MnCO_3$, is far more common than alabandite, MnS, which suggests that the hydrothermal ratio is nearly always less than $10^{-5.1}$.

The extreme lower limit is defined by lead because cerussite, $PbCO_3$, is unknown as a primary mineral. Cobalt is probably not a good element with which to evaluate this ratio because CoS is merely an approximation for the more complex sulfides; therefore, the ratio calculated must represent a maximum possible value. The common occurrence of siderite, $FeCO_3$, in some deposits shows that the ratio must have been less than $10^{-7.7}$, otherwise pyrrhotite would have formed instead.

The $a_{S^-}/a_{CO_3^-}$ ratio can be converted to a ratio of the thermodynamic partial pressures (fugacities) of hydrogen sulfide and carbon dioxide from the following relations:

$$CO_{2(g)} = CO_{2(aq)} \qquad K_{CO_2} = \frac{a_{H_2CO_3}}{P_{CO_2}} = 10^{-1.5}$$

$$H_2S_{(g)} = H_2S_{(aq)} \qquad K_{H_2S} = \frac{a_{H_2S(aq)}}{P_{H_2S}} = 10^{-1.0}$$

$$H_2CO_3 = 2H^+ + CO_3^- \qquad K_{H_2CO_3} = \frac{a^2_{H^+} \cdot a_{CO_3^-}}{a_{H_2CO_3}} = 10^{-16.7}$$

$$H_2S_{(aq)} = 2H^+ + S^- \qquad K_{H_2S(aq)} = \frac{a^2_{H^+} \cdot a_{S^-}}{a_{H_2S(aq)}} = 10^{-21.0}$$

Substituting these into a single equation gives

$$\frac{P_{H_2S}}{P_{CO_2}} = 10^{3.8} \frac{a_{S^-}}{a_{CO_3^-}}.$$

The P_{H_2S}/P_{CO_2} ratio then becomes $10^{-1.3}$ for the MnS-$MnCO_3$ boundary and $10^{-3.9}$ for the FeS-$FeCO_3$ boundary.

In summary, the $a_{S^=}/a_{CO_3^=}$ ratio at the time of deposition is usually less than 10^{-5} and is commonly as low as about 10^{-8}. Because siderite is relatively more common than alabandite, the region of hydrothermal environments probably extends farther to the siderite side of the FeS-$FeCO_3$ boundary than it does to the alabandite side of the MnS-$MnCO_3$ boundary (fig. 1). Iron and manganese are both almost always present in hydrothermal ore deposits; therefore, the commonness of occurrence of siderite relative to alabandite reflects the anionic composition of the ore-forming fluids rather than the geochemical abundance of the cations.

$a_{CO_3^=}/a_{SO_4^=}$ ratio.—This ratio is the most closely defined of those presented. Barite, $BaSO_4$, is the most common barium mineral in hydrothermal deposits, whereas witherite, $BaCO_3$, is only rarely observed; therefore, the ratio is generally less than $10^{0.0}$. Strontium minerals are not abundant in vein deposits, and either celestite, $SrSO_4$, or strontianite, $SrCO_3$, may occur. Anhydrite, $CaSO_4$, is not common as a hydrothermal mineral, but it may be abundant when found. (For the purpose of this investigation the difference between gypsum and anhydrite plus water is negligible.) As calcite is much more common than anhydrite, the ratio is generally greater than $10^{-4.0}$. Because of the possibility of loss of CO_2 and oxidation of sulfide to sulfate, hot spring environments may have much lower ratios.

$a_{CO_3^=}/a^2_{F^-}$ ratio.—Only one fluoride, fluorite, is common in vein deposits, and it is usually accompanied by calcite. This gives a ratio of $10^{1.6}$, which must be fairly close to the lower limit because SrF_2 (ratio less than $10^{-0.1}$) does not occur. The upper limit is unknown.

$a_{SO_4^=}/a^2_{F^-}$ ratio.—This ratio is poorly defined as greater than $10^{3.0}$ by the SrF_2-$SrSO_4$ boundary as the fluoride does not occur. The upper limit is unknown.

Ratios involving chloride.—None of the ratios involving chloride is useful in this study of hydrothermal processes. Silver, lead, and copper form the only usable insoluble chlorides and these same metals also form extremely insoluble sulfides. Therefore the ratios in the ore fluids are probably far removed from the chloride-sulfide boundaries given in Figure 1.

$a_{S^=}/a^2_{OH^-}$ ratio.—The extreme upper limit for this ratio cannot be defined with the present data as all of the metals for which calculations have been made generally prefer sulfides to oxides in hydrothermal environments. This merely restates the geochemical principal that most metals found in hydrothermal deposits are chalcophile rather than lithophile. An upper limit could be calculated from the UO_2-US_2 or SnO_2-SnS_2 boundaries if the data for the sulfides were available.

The ratio must attain values greater than $10^{0.5}$ in order for pyrrhotite and quartz to be deposited together. Stannous tin is unsatisfactory in evaluating ratios because it occurs in complex stannous sulfides for which data are unavailable. Magnetite also is a poor compound on which to generalize because its occurrence in hydrothermal environments is generally

restricted to high-temperature deposits where extrapolation of the low-temperature data is most uncertain.

The ratio must go as low as $10^{-2.4}$ in order that the rare mineral pyrochroite, $Mn(OH)_2$, may form, and must also be less than $10^{-2.0}$ for rhodonite, $MnSiO_3$, to precipitate instead of alabandite and quartz. Zincite, ZnO, and willemite, Zn_2SiO_4, are very rare hydrothermal (?) minerals that occur in abundance at Franklin, New Jersey, in association with trace amounts of complex lead silicates. This suggests that the $a_{S^-}/a^2_{OH^-}$ ratio may only very rarely be as low as $10^{-8.7}$ (assuming that the more complex lead silicates are sufficiently stable to raise their effective ratios to that of ZnS-ZnO or $10^{-8.7}$).

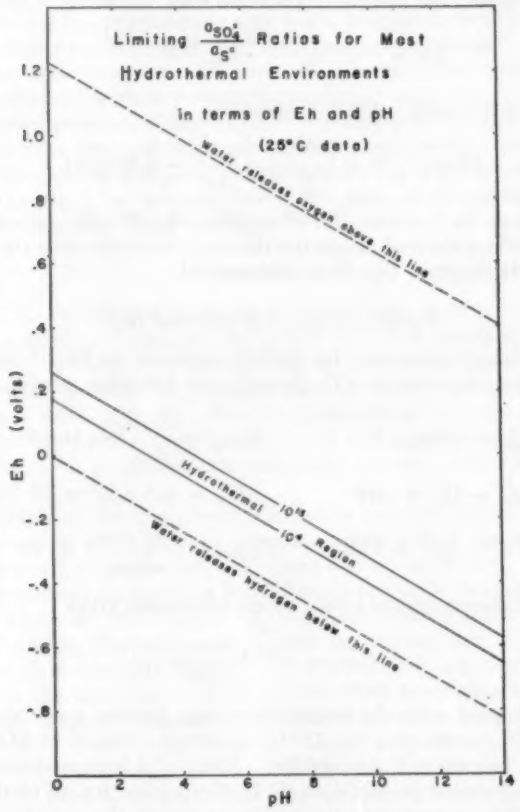
As the deposit at Franklin has long been a puzzle to geologists, it is interesting to point out some of the unique features of these calculations regarding this type of mineralization. The ore body is characterized by high-grade zinc-manganese-iron ore of complex mineralogy with very little lead or copper and only traces of sulfides. The ore minerals are chiefly franklinite, $(Fe, Mn, Zn)O \cdot (Fe, Mn)_2O_3$, willemite, Zn_2SiO_4, tephroite, Mn_2SiO_4, and zincite, ZnO. Various theories of origin have been advanced ranging from metamorphism of sedimentary ores, to metamorphism of an oxidized epigenetic deposit, to hydrothermal activity, but none of these explanations seems fully satisfactory. Figure 1 shows that the three metals most likely to be precipitated as the oxides rather than as sulfides (neglecting stannous tin because it is generally oxidized to cassiterite) are manganese, iron and zinc—the three ore metals at Franklin. Another interesting feature is that although most zinc ores carry appreciable quantities of cadmium, there is little of it at Franklin. This feature also shows up prominently in Figure 1 where cadmium has a sulfide to carbonate ratio very similar to lead and zinc, while the sulfide to hydroxide ratio for cadmium is close to that of lead and far from that of zinc. Thus, although the mechanism of transport and deposition of the Franklin type of ores is still unexplained, the mineralogy falls very nicely into an undefined scheme whereby the $a_{S^-}/a^2_{OH^-}$ ratio was unusually low at the time of deposition. Of course, the ratios calculated here are, at best, very crude approximations of the actual ratios for such a high temperature deposit as Franklin.

$a_{CO_3^-}/a^2_{OH^-}$ ratio.—For siderite and quartz to precipitate together the ratio must be at least $10^{8.3}$, and the coexistance of hematite and siderite pushes the ratio above $10^{8.7}$. For rhodonite, $MnSiO_3$, to form instead of rhodochrosite and quartz the ratio must be less than $10^{9.1}$. Because wollastonite, $CaSiO_3$, does not generally take the place of calcite plus quartz under hydrothermal conditions, $10^{9.7}$ must be a lower limit for this ratio except for rare, silica-deficient environments where the value must be below $10^{9.6}$ for pyrochroite to form in preference to rhodochrosite.

$a_{SO_4^-}/a_{S^-}$ ratio.—This ratio is of particular interest because it provides a way to estimate the oxidation potential, Eh, of hydrothermal environments. Unfortunately, this ratio cannot be closely defined directly because most elements that tend to form insoluble sulfates do not form insoluble sulfides. An exception is lead, but the sulfide is so much less soluble than the sulfate that no significant data are obtained. However, by using the $a_{S^-}/a_{CO_3^-}$ and $a_{CO_3^-}/a_{SO_4^-}$ relations, some idea of the maximum and minimum

values for the $a_{SO_4^=}/a_{S^=}$ ratio may be obtained. If a reasonable range of values for the $a_{S^=}/a_{CO_3^=}$ ratio is taken as from 10^{-4} to 10^{-10}, and similar values are taken for $a_{CO_3^=}/a_{SO_4^=}$ as from 10^{0} to 10^{-5}, it is readily apparent that the greatest reasonable range for the $a_{SO_4^=}/a_{S^=}$ ratio is from 10^{4} to 10^{15}. This is a large variation, but is not unreasonable in view of the possibility of oxidation of sulfide to sulfate by reaction with oxygenated groundwaters

Figure 4



and the concomitant change in pH. As shown in Figure 4, this gives a very narrow band on the Eh-pH diagram.

The following equation is the one of interest in this consideration: $S^{=} + 4H_2O = SO_4^{=} + 8H^{+} + 8e^{-}$. To find the Eh of this system the usual electrochemical equation is applied:

$$E = E^{0} - \frac{RT}{nF} \ln \frac{a_{SO_4^=} \cdot a^{8}_{H^+}}{a_{S^=}},$$

where R is the gas constant, T the absolute temperature, E the electromotive force of the system considered, E^0 the electromotive force when all constituents are at unit activity, and nF the number of Faradays. Because Eh equals $-E$,

$$\mathrm{Eh} = -E^0 + \frac{RT}{nF} \ln \frac{a_{SO_4^{=}} \cdot a^8_{H^+}}{a_{S^-}}$$

on substituting and converting to common logs,

$$\mathrm{Eh} = -E^0 + \frac{0.059}{8} \log \frac{a_{SO_4^{=}} \cdot a^8_{H^+}}{a_{S^-}}.$$

By definition pH equals $-\log a_{H^+}$; therefore,

$$\mathrm{Eh} = -E^0 + \frac{0.059}{8} \log \frac{a_{SO_4^{=}}}{a_{S^-}} - 0.059\ \mathrm{pH}.$$

From data given by Latimer (9), E^0 equals -0.148 volt. By substituting the limiting values derived above for the $a_{SO_4^{=}}/a_{S^-}$ ratio into this last equation the Eh-pH diagram (fig. 4) is constructed.

Partial Pressures of CO_2 and H_2S

The $a_{CO_3^{=}}/a^2_{OH^-}$ ratio may be directly equated to the thermodynamic partial pressure (fugacity) of CO_2 through the following relations:

$$CO_{2(g)} = CO_{2(aq)} \qquad K_{CO_2} = \frac{a_{H_2CO_3}}{P_{CO_2}} = 10^{-1.5}$$

$$H_2O = H^+ + OH^- \qquad K_w = a_{H^+} \cdot a_{OH^-} = 10^{-14.0}$$

$$H_2CO_3 = 2H^+ + CO_3^{=} \qquad K_{H_2CO_3} = \frac{a^2_{H^+} \cdot a_{CO_3^{=}}}{a_{H_2CO_3}} = 10^{-16.7}$$

Substituting these equations into a single expression gives

$$P_{CO_2} = 10^{-9.8} \frac{a_{CO_3^{=}}}{a^2_{OH^-}}.$$

This figure, coupled with the reasonable range for the $a_{CO_3^{=}}/a^2_{OH^-}$ ratio of from 10^2 to 10^{10}, would give (at 25° C) a partial pressure of CO_2, which is almost always less than 1 atmosphere. Even at a temperature of 200° C, the P_{CO_2} (as calculated from the van't Hoff equation for all of the activity product constants except that for water for which the empirical data are used, see Figs. 2, 3) ranges at least from $10^{-2.7}$ to $10^{0.7}$ atmospheres as determined from the $MnCO_3 + SiO_2 - MnSiO_3$ and $FeCO_3 + Fe_2O_3 - Fe_3O_4$ boundaries, respectively. If it may be assumed that most hydrothermal environments represent points on a *continuous* "spectrum" of CO_2 pressures, it can be concluded that a dense CO_2 phase, such as has been suggested for the Colorado Plateau uranium deposits by Garrels and Richter (5), is not the ore-forming fluid for most hydrothermal deposits. A dense CO_2 phase

would require a high pressure of CO_2; and, since $MnSiO_3$ could not precipitate from such a system ($MnCO_3$ would form instead), it is evident that pressures of CO_2 sufficiently high to form a dense CO_2 phase do not exist in all hydrothermal fluids. Therefore, as sulfide ores are associated with rhodonite in some deposits and with siderite in others, it is concluded that a dense CO_2 phase is not essential for transport of these ores. The occurrence of liquid CO_2 in fluid inclusions at room temperature (P_{CO_2} about 73 atm or more) is generally restricted to those minerals from igneous and metamorphic rocks, pegmatites, and high temperature veins where the application of the room temperature data is most uncertain.

A similar derivation for H_2S gives $P_{H_2S} = 10^{-6.0}(a_{S^=}/a^2_{OH^-})$ at 25° C. If this is combined with a reasonable $a_{S^=}/a^2_{OH^-}$ ratio (fig. 1) of $10^{1.0}$, the resulting partial pressure of H_2S is $10^{-5.0}$ atmosphere. This is in agreement with the fact that liquid H_2S has never been found in fluid inclusions. An increase in temperature slightly increases the P_{H_2S} (calculated in the same manner as the P_{CO_2}), but even at 200° C the pressure remains several orders of magnitude less than one atmosphere.

DISCUSSION

It is not to be inferred from these calculations that the ore-depositing fluids have a fixed composition, but rather that it is possible to place some limits on their variability. The principle used to evaluate the ratios is valid at any temperature or pressure, but the data presented here are certainly to be viewed critically when extrapolated far into the environments of ore deposition. Reliable thermodynamic and chemical data for elevated temperatures and pressures are definitely worthy subjects for further investigation.

The problem of changing from relative to absolute values for the anions discussed does not have an easy solution. However, if the activity of one of the anions can be evaluated, the others can be calculated. To illustrate this it is convenient to specify a hypothetical ore body having the following somewhat idealized mineralogy: galena, sphalerite, alabandite, quartz, rhodonite, calcite, rhodochrosite, anhydrite, barite, and fluorite. If for the moment it is assumed that all of these minerals are deposited in equilibrium from the same solution and if the room-temperature data may be extrapolated to this "deposit," the following ratios may be evaluated: $a_{S^=}/a_{CO_3^=} = 10^{-5.1}$, $a_{CO_3^=}/a_{SO_4^=} = 10^{-3.9}$, $a_{CO_3^=}/a^2_{F^-} = 10^{1.4}$, $a_{SO_4^=}/a^2_{F^-} = 10^{5.3}$, $a_{S^=}/a^2_{OH^-} = 10^{-2.0}$, and $a_{CO_3^=}/a^2_{OH^-} = 10^{3.1}$. If it is further assumed that the pH at the time of deposition is 7.0 and that activity equals concentration, the following concentrations are calculated: $OH^- = 10^{-7.0}$, $F^- = 10^{-6.2}$, $CO_3^= = 10^{-10.9}$, $SO_4^= = 10^{-7.0}$, and $S^= = 10^{-16.0}$. The partial pressures of CO_2 and H_2S are $10^{-6.7}$ and $10^{-8.0}$ atmospheres, respectively. From the $a_{SO_4^=}/a_{S^=}$ ratio the calculated Eh is −0.20 volt. If the calculations are carried one step further so that the activities of the cations are also evaluated, the solution appears impossibly rich in Ca^{++} and improbably rich in Ba^{++} and Mn^{++}. However, if the same mineral assemblage is assumed to have precipitated at 125° C instead of at room temperature, some very

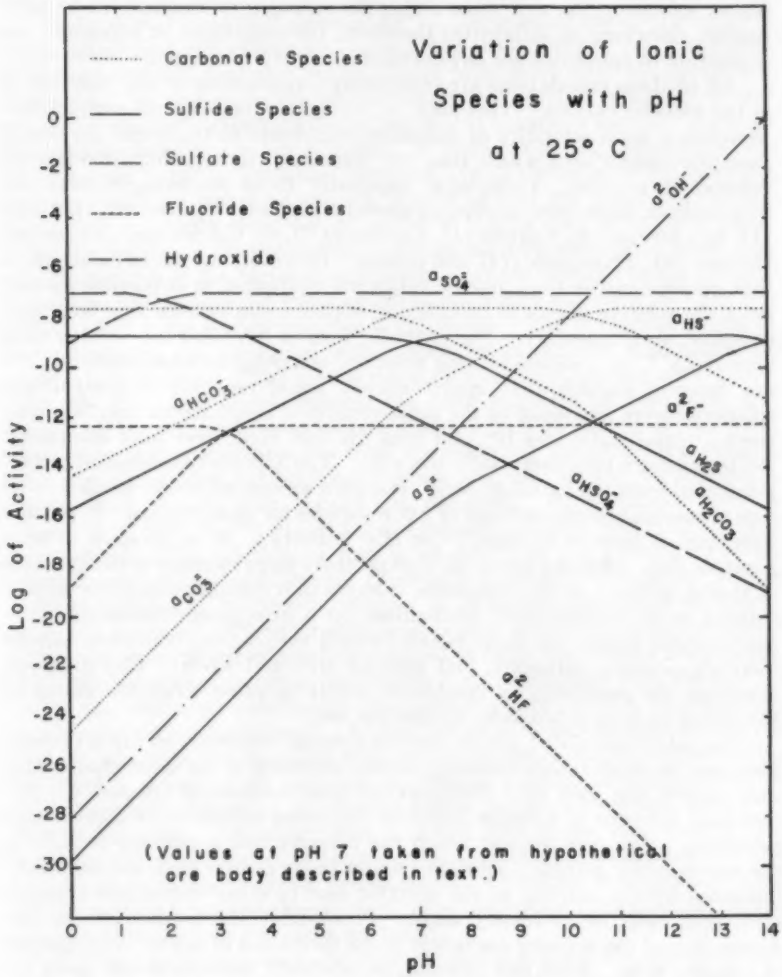
reasonable values are derived. By using the empirical data for the ionization constant of water and the van't Hoff equation to extrapolate the other activity product constants, and assuming a pH of 7.0 (which is slightly basic due to the increased ionization of the water), the following activities are calculated: $OH^- = 10^{-4.9}$, $CO_3^= = 10^{-7.3}$, $SO_4^= = 10^{-3.6}$, $S^= = 10^{-10.7}$, $F^- = 10^{-3.8}$, $Ca^{++} = 10^{-1.6}$, $Mn^{++} = 10^{-3.1}$, $Ba^{++} = 10^{-4.3}$, $Zn^{++} = 10^{-0.7}$, and $Pb^{++} = 10^{-11.7}$. The partial pressures of CO_2 and H_2S are $10^{-4.2}$ and $10^{-6.0}$ atmospheres, respectively. In actual mineral deposits there is generally a definite paragenetic sequence and therefore the assumption that all of the minerals precipitate from the same solution is certainly not warranted. However, many instances exist where two or more minerals were apparently deposited simultaneously and thus some of the ionic activity ratios can be estimated. There are far too many unevaluated variables at present to apply precise calculations, such as those illustrated above, to any real ore body; but it is possible to generalize, as has been done in Figure 1, with the realization that continual refinements must be made as additional data become available. It is noteworthy that the relatively neglected gangue minerals provide most of the information; whereas the much sought, and often voluminously described, ore sulfides reveal little of the nature of the depositing solutions.

The composition of primary fluid inclusions in minerals from ore deposits provides one of the best methods to get absolute values for the concentration of various anions. However, even if adequate analytical procedures are developed, the high concentration of salts common in fluid inclusions (13) makes it unlikely that the activities can be directly equated to concentration without some evaluation of activity coefficients. Perhaps the hydroxyl ion activity during deposition can be defined from wallrock alteration or from conditions of precipitation of wurtzite and marcasite instead of sphalerite and pyrite.

Changes in pH have various effects on the ratios. Figure 5 presents the way each anion will vary in a closed system assuming that some magic mechanism alters pH only. The ratios for this diagram at pH 7 were chosen from the hypothetical ore body described above. A rise in pH slightly increases the $a_{S^=}/a_{CO_3^=}$ ratio and $MnCO_3$ would tend to convert to MnS, but the effect is small until the pH exceeds 11. However, the effect on the ratios involving either, but not both, $SO_4^=$ or F^- is pronounced. These two ions are not appreciably added to by the dissociation of other species in the way that HCO_3^-, HS^-, H_2O, etc. contribute to $CO_3^=$, $S^=$, and OH^-. Therefore, $CaSO_4$ and CaF_2 would tend to be replaced by $CaCO_3$. $MnSiO_3$ would also tend to form from MnS and $MnCO_3$. A decrease in pH would reverse the trends brought on by increasing pH except that there would be little tendency for carbonates, sulfides, silicates or hydroxides to interact below pH 7 because the ratios remain essentially constant.

It is evident in any natural system where precipitation of minerals is occurring that some of the anions may be depleted relative to others. In this way the cations exert a buffering action on changes in the anionic ratios. Iron and calcium are the most important buffers, followed by manganese, barium and strontium.

Figure 5



These calculations determine the compound that will be preferred if a precipitate forms, but they do not predict whether or not a precipitation will occur. This fact, plus the observation that almost any hydrothermal mineral may, on occasion, replace any earlier mineral (hydrothermal or otherwise), suggests that the conditions of deposition and transport are not necessarily separated by an irreversible physico-chemical barrier. Thus, the conditions that are formulated for deposition may also be fair approxi-

mations of the environment of transport. For example, when galena replaces sphalerite the zinc must return to solution, presumably to be redeposited elsewhere as sphalerite; therefore, the conditions of transport and deposition of sphalerite are not necessarily widely divergent.

All of these calculations are completely independent of any complexing of the metallic cations. Therefore, an appeal can be made to complex ions to attain a total solubility of sufficient magnitude to transport the metals (and the anions with which they are combined) in a geologically feasible volume of solution. Complexes, especially those involving sulfide and hydrosulfide, have been applied to geologic problems by Becker (1), Smith (11, 12), Dreyer (2), Garrels (3), Krauskopf (7, 8), Garrels and Dreyer (4), Hemley (6), Thompson (14) and others. By reversing the calculations so that cationic rather than anionic ratios are evaluated, it is possible to estimate the relative degree of complexing between two sulfides that were precipitated simultaneously. For example, lead is 10^3 times less soluble than zinc at 25° C in a sulfide-bearing solution, assuming no complexes. If the ore textures suggest that approximately equal amounts of galena and sphalerite were deposited at the same time, it is necessary to conclude that the $a_{Zn^{++}}/a_{Pb^{++}}$ ratio was 10^3, and thus the lead must have been complexed 10^3 times more effectively than the zinc. The low partial pressure of H_2S calculated from the $a_{S^-}/a^2_{OH^-}$ ratio presents a serious objection to the formation of soluble complex sulfides or hydrosulfides for most metals. (Complex formation is favored by high S^- or HS^- activity.) If an increase in temperature does not bring about an unexpectedly large increase in the pressure of H_2S or stability of the complexes, it seems that complex sulfides or hydrosulfides as an ore-transport mechanism (at a geologically reasonable pH) can be called on only for those metals forming very stable complexes, namely mercury, arsenic, antimony, and perhaps gold and silver. This does not eliminate the possibility of complexes involving other oxidation states of the sulfur such as polysulfide, thiosulfate, etc.

The ratios calculated can be used as a strong argument in favor of complex ions for most sulfide-forming metallic elements in the ore-forming fluid and against the idea that transport for most sulfides is effected by tremendous volumes of solution aided by increased solubility at higher temperatures. The core around which the complex ion hypothesis is built is the necessity for getting a solubility many times greater than the solubility indicated by the activity of the metallic ion; in other words, the activity coefficient must be extremely small. Presumably the mechanism for the diminution of the activity coefficient is the formation of one or more species of complex ions. With this in mind, an ore body (such as might easily be found in the low temperature Mississippi Valley type deposits) is chosen which contains equal amounts (in moles) of calcite, barite, sphalerite, and galena. The solution from which these minerals precipitate is assumed to have the same anionic composition as the previously discussed hypothetical ore body, i.e., $CO_3^- = 10^{-7.3}$, $SO_4^- = 10^{-3.6}$, and $S^- = 10^{-10.7}$, at a temperature of 125° C. The activities of the cations of interest are: $Ca^{++} = 10^{-1.6}$, $Ba^{++} = 10^{-4.3}$, $Zn^{++} = 10^{-9.7}$, and $Pb^{++} = 10^{-11.7}$. *If* the actual concentration of lead in the solution were equal to the Pb^{++} activity, i.e., no lead

complexes, it would require $10^{11.7}$ liters of solution to transport one mole of lead.[3] This same volume of solution would transport $10^{10.1}$ moles of Ca^{++}, $10^{7.4}$ moles of Ba^{++} and $10^{2.0}$ moles of Zn^{++}. Since equal amounts of calcite, barite, sphalerite, and galena are deposited in the ore body, vast quantities of calcium, barium, and zinc would remain in solution after the deposition of the ore. In this event the excess calcite, barite, and sphalerite would either be deposited somewhere else or be released to surface waters. Because barite and sphalerite are not abundant in most hot-spring deposits (which are presumed to be the "outcrop" of recent hydrothermal activity) or in the solutions flowing from these springs, it follows that the major part of the barite and sphalerite must be deposited at depth, i.e., in the ore body. Thus, the volume of the ore-forming solution must be sufficiently small that no large portion of the barite or sphalerite is carried through to the surface. Therefore, lead cannot be transported in quantities sufficient to form ore bodies unless some sort of complex is employed. The numerical values in this calculation can be varied within wide limits without weakening the argument in the least. The metals mercury, antimony, arsenic, silver, gold, cadmium, zinc, and copper present the same situation as does lead, and complexes are required for adequate transport. The nature of the complexes is open to speculation, but from the preceding paragraph it is evident that complex sulfides and hydrosulfides are probably inadequate to explain the behavior of lead, zinc, copper and cadmium. Other cations such as Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, and Mn^{++} are probably transported in an uncomplexed state. The position of iron is uncertain as the solubilities of its minerals are intermediate between those of the definitely complexed metals and the probably uncomplexed metals. In summary, the metals that form extremely insoluble sulfides must be transported as complex ions; otherwise the tremendous volume of solution required to carry the sulfides would wash away the more soluble carbonates, sulfates, etc. associated with the ore.

In the course of calculating the anionic ratios several incompatible mineral pairs were established. It has been mentioned already that pyrochroite and quartz are unstable with respect to the formation of rhodonite. Some other incompatible pairs are: siderite-alabandite, anhydrite-strontianite, anhydrite-witherite, celestite-witherite, siderite-rhodonite, and pyrrhotite-rhodonite. Assuming that thermal effects do not change the relations, the nonexistance of incompatible assemblages would support the premise of equilibrium during precipitation. Of course it is probable that the depositing solutions change with time, and thus incompatible phases possibly may occur in the same ore body.

This discussion has been directed primarily toward the interpretation of hydrothermal deposits. But the principle applies equally well to any precipitation or replacement, i.e., the syngenetic deposition of metallic sulfides or carbonates in sediments or the formation of secondary minerals

[3] Krauskopf (7) has discussed this point for mercury deposits in terms of geologically feasible volumes of solution and concludes that the absolute minimum concentration of the metal is 0.0001 ppm. Thompson (14) calculated a minimum figure of about 0.1 ppm which seems to be more realistic, at least for mercury deposits. Both Krauskopf and Thompson conclude that complexes are important.

in the oxidized zone. For example, calcite will precipitate from sea water only so long as the $a_{CO_3^{=}}/a_{SO_4^{=}}$ ratio is greater than $10^{-3.9}$; below that value anhydrite (or gypsum) will be deposited. Considering the oxidized zone, it is noted that if the $a_{S^{=}}/a_{CO_3^{=}}$ ratio is about 10^{-16} sphalerite will tend to convert to smithsonite, $ZnCO_3$, and at the same time greenockite, CdS, will precipitate as the cadmium is released from the sphalerite. Likewise, from the $a_{S^{=}}/a^2_{OH^-}$ ratios, it is seen that silver, copper, and mercury may either be retained as sulfides or form secondary sulfides even though the manganese, iron, zinc and lead sulfides have converted to oxidized minerals.

Many more data must be accumulated before the ratios can be rigorously evaluated for individual deposits, and even more work is required before actual composition of the ore-bearing solution is known. Data for elevated temperatures are essential. Calculations of solubility which involve extrapolation of low-temperature data such as those of Verhoogen (15), as well as those presented in this paper, must be tested by experimental work.

CONCLUSIONS

On the basis of thermodynamic data at 25° C some limits on the variability of several anionic ratios in the ore-forming fluid have been calculated. This technique can contribute very significant information toward the understanding of the genesis of ore deposits, but additional data at higher temperatures are needed before the final conclusions can be reached. Tentative conclusions are as follows:

1. The ore-depositing solutions are very high in CO_2 relative to H_2S.
2. The pressure of CO_2 is sufficiently low that a dense CO_2 ore-bearing phase is unlikely for most deposits.
3. Complex ions of some type are necessary to transport most of the sulfide-forming metals in the ore solution, though the pressure of H_2S is too low to make it probable that the complex is with sulfide or hydrosulfide ions (except for mercury, arsenic, antimony, and possibly gold and silver).
4. The oxidation potential of deposition (at 25° C) is defined from the sulfate to sulfide ratio for most deposits as: Eh (in volts) = $0.22 \pm 0.04 - 0.059$ pH.
5. These calculations are very useful in explaining the relations between minerals in the oxidized zone or in sedimentary deposits.

ACKNOWLEDGMENTS

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U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.,
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ECONOMIC CONSIDERATION OF PEBBLE PHOSPHATE DEPOSITS OF ALACHUA COUNTY, FLORIDA[1]

E. C. PIRKLE

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ABSTRACT

Most of the pebble phosphate deposits in Alachua County are low-grade and are not considered as commercial at the present time. These deposits, however, add to the reserves of the State of Florida a considerable tonnage of low-grade phosphate that will average at least 50 percent BPL.

Many of the phosphate grains and pebbles of the Hawthorne formation are believed to have formed as discrete individual accretionary aggregates in a marine environment. Other common types represent limestone fragments, marl fragments and shell material in which phosphate has replaced varying amounts of the carbonate content. This replacement apparently took place under marine conditions though in places later action by groundwater may have resulted in a higher grade pebble through the removal of excess calcium carbonate or the replacement of such carbonate by phosphate. The dominant types of phosphate particles in a locality appear to be a factor in "high-grade" as compared to "low-grade" deposits.

INTRODUCTION

THE purpose of this investigation was to determine the economic possibilities of pebble phosphate in Alachua County, Florida. Although pebble phosphate was reported from Alachua County in 1892 by Johnson (3), it was only

[1] This material was included in a dissertation prepared under the direction of the late Dr. John L. Rich and Dr. William F. Jenks. The report was submitted to the Graduate School of the University of Cincinnati to fulfill part of the requirements for the degree of Doctor of Philosophy.

recently realized that large concentrations of such phosphate exist. No reports have been published concerning these accumulations.

Petrographic and chemical analyses show that several basic types of pebbles and grains of phosphate occur and that the economic potential of a deposit is dependent on this hitherto disregarded factor. The dominant types of these pebble phosphate particles were studied.

LOCATION

Alachua County is located in the north-central part of peninsular Florida (Fig. 1). Sellards (7) divided the county into the following major physiographic areas.

FIG. 1. Location of Alachua County, Florida.

(1) A plateau-like region north of Gainesville and including most of northeastern Alachua County.
(2) A western plains region.
(3) An area in the south-central and southeastern part characterized by flat-bottomed lakes, prairies and erosional remnants of the plateau.

These areas can be delimited by an examination of Figure 2. For a further discussion of various topographic features in Alachua County see Pirkle (5).

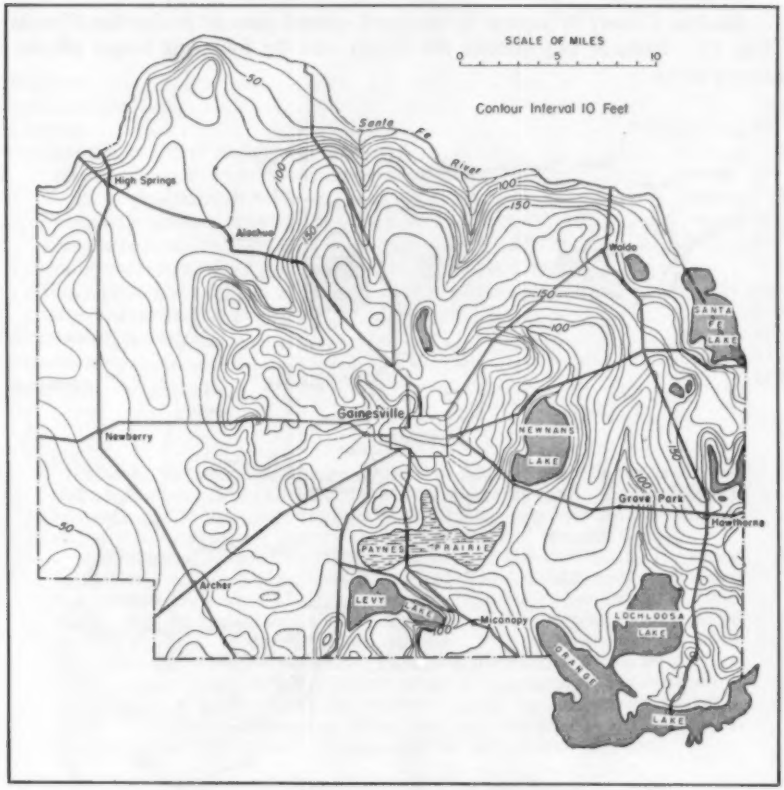

FIG. 2. Topographic map of Alachua County.

GENERAL DISCUSSION OF PHOSPHATIC SEDIMENTS

In Alachua County, pebbles and grains [2] of phosphate occur disseminated through all the sediments of the Hawthorne formation (Middle Miocene) and

[2] Phosphate particles that pass a 20-mesh screen are termed grain size, flotation size, or concentrates. Larger phosphate sediments are considered pebble size. This is partly in conformity with local terminology in the phosphate industry.

as concentrations in lenses and irregular bodies. In some individual beds, the phosphate pebbles and grains, even though present throughout, are more abundant at the top or near the bottom. For a detailed section illustrating the nature of occurrences of phosphorite throughout parts of the Hawthorne formation, see Brooks Sink exposure (6).

Concentrations at Top of Hawthorne Formation

In general, in the plateau area north of Gainesville (east of State Roads 23 and 329) and throughout the northeastern and east-central parts of Alachua

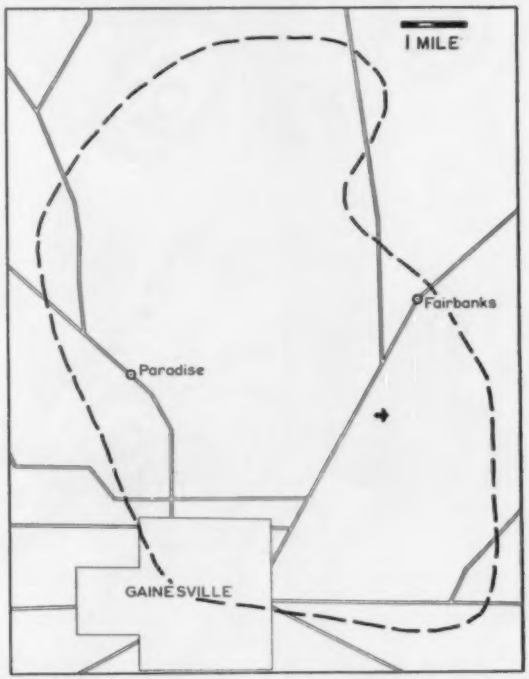

FIG. 3. Location of area containing heaviest phosphate concentrations north and northeast of Gainesville.

County, slight to heavy concentrations of pebbles and grains of phosphate occur at the top of the Hawthorne formation. This top zone of phosphatic sediments varies in thickness from a few feet to 30 or 40 feet and consists largely of pebbles and grains of phosphate embedded in materials ranging from almost pure sand, clay, or carbonate to varying combinations of sand, clay and carbonate. The quantity of phosphate grains and pebbles ranges from slight amounts to as much as 800 tons per acre foot.

These phosphatic sediments are covered by loose sand, clayey sand and sandy clays of Pleistocene age ranging in thickness to 45 feet. In places a shell marl considered by Cooke (2, p. 183) as Upper Miocene in age occurs between the Pleistocene materials and the underlying phosphate concentrations. The heaviest concentrations of phosphate were found in two areas:

FIG. 4. Photomicrographs of individual phosphate grains. Plane polarized light. × 17.

A—Phosphate particle composed of numerous grains of quartz and phosphate (opposite letter A) cemented with phosphate. B—Phosphate grain consisting of abundant quartz and some phosphate particles embedded in phosphate. Note the whitish or grayish phosphate extending from the bottom of the particle and occupying its central part. The outline of this phosphatic material seems to have been controlled to some extent by the quartz and small phosphate grains. C, D, E and F—Phosphate grains showing internal structures. Specimen C is typical of a concretionary oolite.

(1) just north and northeast of Gainesville (Fig. 3), and (2) south of the Hawthorne Highway between the towns of Grove Park and Hawthorne (see discussion of Roy Brown Property in this paper).

The phosphate grains and pebbles in the Hawthorne formation are various shades of white, black, brown, gray, tan, amber and orange. Thin sections

of some of the grains and nodules show concentric zones. Others are uniform throughout. The zones in fresh particles are believed to be due to accretion during deposition (Fig. 4, C), whereas some of those found in weathered surface exposures may have been produced secondarily. Some particles contain non-concentric banding. The photomicrographs of Figure 4 show a few internal structures of individual phosphate grains.

Types of Phosphate Particles

For convenience the following names are used to designate different types of phosphate grains and pebbles.

Concretionary Oolites and Masses.—Accretion was an important factor in the development of these phosphate grains and pebbles. The phosphatic materials of this type have incorporated clastic quartz, orthoclase feldspar, microcline, smaller concretionary particles of phosphate and organic matter. Other inclusions commonly present are diatoms, sponge spicules and unidentifiable fossil fragments. Biotite has been noted in a few phosphate particles. The percentages of impurities vary. Some grains and pebbles show only a few visible inclusions (Fig. 4, C), whereas others contain abundant such clastic material (Fig. 4, A, B). Fossil fragments, noted in some of the concretionary oolites and masses, were not observed to be present in the sediments surrounding such phosphate grains and pebbles. Figure 5 shows a photomicrograph of part of a phosphate pebble.

Aggregated Masses.—Many masses ranging in size from very small particles to pebbles show no plan of growth. These may represent aggregates of colloidal phosphate precipitated directly from sea water. Such materials may have been aggregated on the sea floor and at times apparently were rolled and washed around incorporating within the grains and pebbles various types and amounts of clastic sediments. White grains associated with more massive clays are discussed separately.

Steinkerns.—Numerous phosphate grains and pebbles were formed by deposition of phosphate in the interiors of tiny mollusk shells, chambers of bryozoans (Fig. 6, A; Fig. 7, A) and cavities of skeletons of other invertebrate animals. Grains and pebbles formed by the filling of mollusk shells contain the same general types of inclusions listed for the concretionary oolites and masses.

It appears that some of these steinkerns have resulted from phosphate replacement of infiltrated clastic sediments. This change is comparable, though not analogous, to the diagenetic origin of grains of glauconite found within shells in other deposits.

Replacement of Skeletal Remains.—Fragments of corals, bryozoans, mollusk shells and the teeth and bones of animals have been replaced to varying degrees by phosphate. At times replacement of shell material started from the outside of shell fragments and proceeded into the shell (Fig. 6, C, D; Fig. 7, C, D). In other cases phosphate was deposited within the interiors of shells as explained above for steinkerns, and replacement of the carbonate shells started from the inside.

Replacement of Carbonate in Fragments of Shell Marls and Limestones.—Some phosphatic particles were formed by replacement of shell material and the fine-grained calcareous groundmass in fragments of shell marls and limestones. These particles retain the fragmental structure of the original limestone aggregate. The shell marls and impure limestones consisted originally

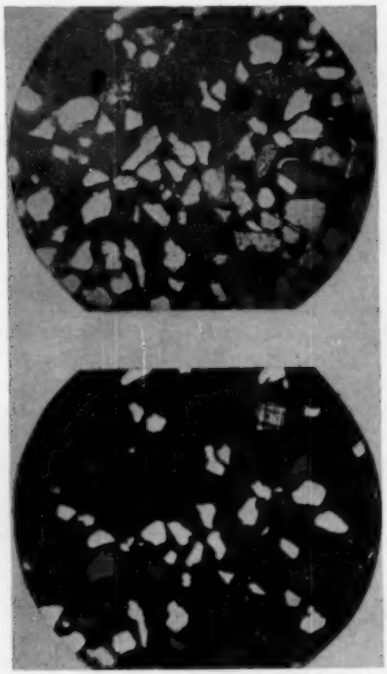

FIG. 5. Photomicrographs of part of a brown phosphate pebble collected from the phosphate concentration at the top of the Hawthorne north of Gainesville. Note the high content of included quartz sand and feldspar, and also several small phosphate grains (black or gray in top photo) included in the large pebble. The top picture was made with plane polarized light; the bottom picture under crossed nicols. × 17.

of fine carbonate, fossils, shell fragments, quartz sand, clay and small concretionary oolites and masses of phosphate.

Phosphate particles resulting from replacement of carbonate in fragments of purer limestones contain less impurities, such as quartz sand, than the pebbles mentioned above. Mingled with phosphatic sediments are commonly found limestone fragments in which only a very small amount, if any, of the carbonate has been replaced by phosphate.

Phosphatic Clay Balls.—Phosphatic clay balls have been noted in many areas of Hawthorne sediments. These normally contain only minor amounts of included material such as quartz sand. Such clay balls may represent, in cases, another form of "aggregated masses" formed on a sand free bottom.

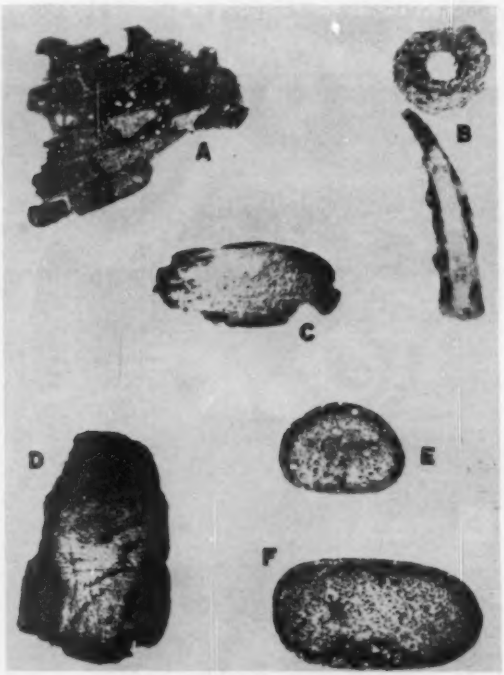

FIG. 6. Photomicrographs of individual phosphate grains. Plane polarized light. × 17.

A—Phosphate grain resulting from filling by phosphate of the zooecial chambers of a portion of a bryozoan colony. B—Spines. Circular fragment is cross section of an echinoid spine. Long particle represents a spine of an unidentified organism. Such spines often are converted to phosphatic sediments by replacement or open-space filling. C and D—Shell fragments of mollusks partly replaced by phosphate. Note the replacement is from the outside of the particle inward. E and F—Phosphate grains containing minute fragments of clastic sediments. Such grains may contain parts of sponge spicules and diatoms and seem to have developed in areas characterized by fine sediments.

Replacement of Feldspar and Quartz.—Occasional grains show feldspar particles replaced by varying amounts of phosphate (Fig. 7, E). In rare cases there are suggestions that quartz grains may have been partly replaced by phosphate. Replacement such as this is usually attributed to syngenetic changes during diagenesis.

Phosphatic Pebbles Resulting from Weathering

Exposure and weathering of Hawthorne sediments containing a high percentage of phosphorite commonly result in the formation of porous pebbles. These pebbles consist largely of quartz sand and phosphate particles loosely cemented by a phosphatic clay. The vugs are thought by Cooke (2, p. 145) to be due to leaching of phosphorite.

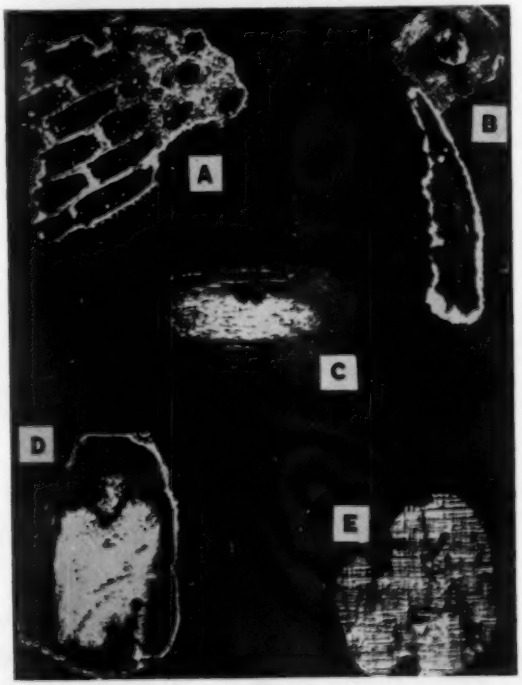

FIG. 7. Photomicrographs of individual phosphate particles. X-nicols. × 17. A, B, C and D—Under X-nicols of grains labeled respectively on Figure 6. E—Microcline partly replaced by phosphate.

Phosphate Particles Associated with More Massive Clays

In those parts of the main body of the Hawthorne characterized by more massive clays, white grains of phosphate are in places mixed with quartz sand, and occur with the quartz sand as stringers in the massive clays or as individual beds or lenses between clay layers. Some of these beds or lenses are as much as 5 feet thick and may contain up to 30 or 40 percent white phosphate grains with the remainder of the lens or bed consisting of quartz sand with only minor amounts of clay.

These white phosphate grains are soft, even plastic when wet and have been found in all cases analyzed to be exceedingly high in phosphate content. For example, white, soft grains separated from an 18-pound sample collected from a clay exposure about 5½ miles west of Gainesville on the north side of the Newberry Highway had an average BPL content of 79.25 percent. The insoluble content was 4 percent, of which 2.54 percent consisted of iron and

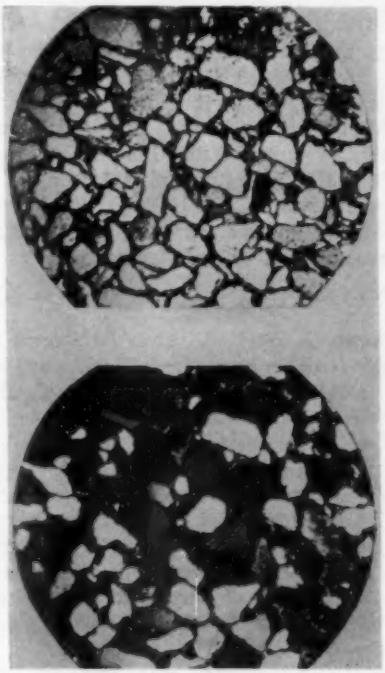

FIG. 8. Thin section of phosphatic sandstone at clay exposure about 5½ miles west of Gainesville on the north side of the Newberry Highway. The rock consists largely of quartz and phosphate grains with minor amounts of clay, feldspar and biotite. It is a lens about 5 feet thick, enclosed by massive clay; phosphate grains are white and soft. Some of them have been compressed so as to fit tightly against other grains. Phosphate of this type in all cases checked has been of high grade. Top photo with plane polarized light; lower with X-nicols. × 17.

aluminum oxides. White and gray pebbles from this same sample had an average BPL content of 72.04 percent with a content of insoluble material amounting to 10.51 percent of which 3.39 percent was iron and aluminum oxides. These analyses were furnished by the American Metal Company, Limited.

Thin sections (Fig. 8) show no structure in the grains of white phosphate

and very few inclusions of visible clastic minerals. During weathering, those loose white grains that are associated with quartz sand at times appear to harden, in some cases apparently changing to a more brownish color.

This same type of soft phosphate grains commonly occurs disseminated through massive clay. It may be that during weathering the white phosphate reacts chemically with the enclosing clay to form a phosphatic clay.

ECONOMIC CONSIDERATION OF ALACHUA COUNTY PEBBLE PHOSPHATE

Before discussing the economic possibilities of the pebble phosphate in Alachua County, a few problems and trends in the phosphate industry of Florida will be considered. Most of the phosphate produced in Florida comes from the Bone Valley field in Polk and Hillsborough counties. Its average grade is approximately 74 percent BPL (Bone Phosphate of Lime).

About two-thirds of the agricultural phosphate needs of this country are met with normal superphosphate, $Ca(H_2PO_4)_2$ mixed with calcium sulfate, which is produced by treating finely ground phosphate rock with sulphuric acid. The general reaction may be indicated as follows:

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4$$

Only one acidulation step is involved. Over 90 percent of the rock used in the manufacture of this fertilizer comes from Florida, making that industry the big consumer of Florida phosphate rock. The south always has been the leading consuming area of this fertilizer.

During the earlier days in the history of the normal superphosphate industry, rock was mined in Florida and shipped by low-cost ocean transportation to manufacturing plants concentrated along the Eastern seaboard. Because the farm market extends inland from such plants and the demand for fertilizers increased with progressive agricultural practices, plants have later been constructed in a number of states, i.e., Ohio, Illinois, Kentucky and Tennessee. In the manufacture of normal superphosphate, it is more economical, because of freight and storage costs, to use phosphate rock with a BPL content of 75 percent or greater.

With the increase of fertilizer needs in the midwest, particularily after the development of hybrid corn, the need for a more concentrated fertilizer to help overcome the cost on long freight hauls became more acute. The triple superphosphate industry developed partly in response to this need. Triple superphosphate plants naturally were built near the source of the rock so that a concentrated product could be shipped.

Between 1948 and 1953 the amount of triple superphosphate produced in the United States doubled, and today this product supplies over 20 percent of the agricultural phosphate needs of the country. As most of the rock used in the manufacture of this product comes from Florida, the consumption of Florida phosphate rock for that use has been increasing greatly in the past few years. The higher concentration of phosphate in triple superphosphate results in savings on storage and shipping costs for the producer. Also, the greater concentration of available plant food in this fertilizer furnishes definite

advantages for some farming operations. Some high-analysis fertilizers, such as the popular 5–20–20, cannot be made with normal superphosphate. Such a fertilizer requires triple superphosphate.

Two acidulation steps are used in the manufacture of triple superphosphate. In the first step, sulphuric acid is added to phosphate rock to yield a weak phosphoric acid (H_3PO_4). This, then, is usually concentrated by evaporation. In the second step, rock is treated with the phosphoric acid, resulting in triple superphosphate. The most important chemical changes are indicated by the following reactions.

$$2Ca_3(PO_4)_2 + 6H_2SO_4 + 12H_2O \rightarrow 4H_3PO_4 + 6CaSO_4.2H_2O$$
$$Ca_3(PO_4)_2 + 4H_3PO_4 + 3H_2O \rightarrow 3Ca(H_2PO_4)_2.H_2O$$

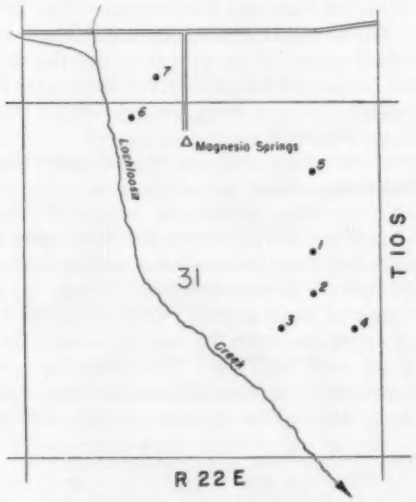

FIG. 9. Location of borings on Roy Brown Property.

The resulting product, triple superphosphate, contains almost three times the amount of available P_2O_5 as normal superphosphate.

In the manufacture of triple superphosphate, low-grade phosphate rock (BPL approximately 68 percent) can be used economically in the first acidulation step. This step consumes about two-thirds of the phosphate rock needed in the production of that product. Although some companies still are using high-grade rock for both steps in the manufacture of triple superphosphate, it should be noted that other companies are utilizing low-grade rock in the first acidulation step.

With most phosphate-rock-producers faced with depletion of their high-grade rock reserves within 20 years at the present rate of production, and with the rapid growth of industries, such as triple super, electric furnace acid, and

wet process acid capable of utilizing low-grade rock efficiently, it is believed that the average grade of phosphate rock produced in Florida will decrease steadily. As the high-grade land pebble phosphate is being depleted rapidly, it is certain that the phosphate-rock-producers will be faced in the future with the necessity of using lower grade rock if they continue to mine pebble phosphate in Florida.

Descriptions and Analyses of Borings on Roy Brown Property

It was decided to select one of the areas of phosphate concentration in Alachua County and test it by using the same methods of prospecting utilized in the commercial Bone Valley district. The area selected for this check was in the region of phosphate concentration south of the Hawthorne highway and between the towns of Grove Park and Hawthorne. This is Dall's type locality of the Hawthorne. The program was carried out through the courtesy of Mr. Roy Brown, the present owner of the property, and the drilling was done by the American Metal Company, Limited. Seven holes were drilled by means of hand augers. Phosphate analyses were run on holes 1 through 5. For the location of the holes, see Figure 9.

For the purpose of phosphate analyses, holes 6 and 7 were blanks. These two holes were drilled in an attempt to encounter an undisturbed lens of *Ostrea normalis* Dall, a characteristic Hawthorne fossil. These fossils were encountered in hole 6, but it can not be proved that they represent an undisturbed lens. The sites for the two holes were selected near Lochloosa Creek where it was believed the phosphate concentration would not be encountered, thus eliminating the necessity of hand augering through additional sediments.

On the following pages are listed the logs of holes 1 through 5. Laboratory analyses are given with each log. The following terms used with the logs are standard terminology in the commercial Bone Valley field and are used with the following meanings in reference to this drilling.

Overburden—Sediments overlying phosphate concentration.
Matrix—Sediments containing abundant phosphate particles. This term refers to the economic part of the phosphatic sediments in the Bone Valley district.
Bed Clay—Sediments (with high content of clay) underlying the heavy concentration of phosphate grains and pebbles.

The following abbreviations are used in the analyses data:

(*X*/*Y*)—Ratio of overburden to matrix. *X* feet of overburden to *Y* feet of matrix.

Plus 14—Pebbles retained on 14-mesh screen.

14/20—Pebbles that passed the 14-mesh screen and were retained on 20-mesh screen.

Conc.—Concentrates. Grains larger than 150-mesh that passed 20-mesh screen. Flotation size sediments.

Product—Total product. Derived by adding all plus 14, 14/20, and concentrates.

T/A Ft.—Tons per acre foot.

T/A—Tons per acre.

BPL—Bone phosphate of lime, P_2O_5 times 2.185.

Insol.—Insolubles in various mesh sizes.

HOLE 1—ROY BROWN PROPERTY

Section 31, T. 10 S., R. 22 E. Log by: E. C. Pirkle

Feet	
	Overburden (Post-Hawthorne)
0 to 1	Dark brown, loose sand with admixed organic matter.
1 to 2	Whitish, loose to slightly clayey sand, some porous pebbles up to 1 by 1½ inches.
2 to 4½	Hard pan. Firm, brown to gray, clayey sand with fragments of sandrock.
4½ to 7	Grayish to whitish, sandy clay or clayey sand.
	*Matrix** (Hawthorne)
7 to 10	Grayish to buff, clayey sand with abundant pebbles and grains of phosphate. Phosphate pebbles and grains are dominantly white, some brown.
10 to 14	Gray to buff, clayey sand or sandy clay with a decrease in pebble size phosphate and an increase in grains of phosphate. Grains of phosphate are white, gray, tan and brown.
14 to 20	Buff, clayey sand with a decrease, but still common grains of brown, tan, and amber phosphate. Bottom foot contains pebbles of brown and gray phosphate.
	Bed Clay (Hawthorne)
20 to 21	Sandy, phosphatic clay with some grains of brown, amber, and black phosphate.
21 to 30	Greenish to greenish gray, massive clay with thin stringers consisting of a mixture of quartz sand and white phosphate grains. Embedded in clay are grains of soft, white phosphate.

Analyses of hole 1: Summary

Hole	Fraction	Test results		
		T/A	BPL	Insol.
1 (7/16½)	plus 14	3381	58.5	16.86
	14/20	1037	60.1	15.09
	Conc.	4771	68.8	4.95
	Product	9189	64.0	10.48
	T/A Ft.	557		

* The thickness of this unit does not correspond to that given with the above analyses of the materials. The log was made from samples collected every 6 inches and examined under a binocular microscope, whereas the samples analyzed were based upon units determined in the field.

HOLE 2—ROY BROWN PROPERTY

Section 31, T. 10 S., R. 22E. Log by: C. O. Ensign

Feet	*Overburden* (Post-Hawthorne)
0 to 1	Black, sandy top soil.
1 to 4	Large rocks. A cobble bed. Cobbles are very hard and show ferruginous seams. The surface appears porous.
4 to 4½	Light gray sand grading into a light sandy clay. This stratum contains some cobbles as above with size decreasing with depth.
4½ to 5½	Intercalated light gray and orange sandy clay containing a trace of white phosphate pebbles and some sandrock pebbles.
5½ to 7	Gray, sandy clay containing sandrock pebbles and a trace of cream and white phosphate nodules.
	Matrix (Hawthorne)
7 to 10	Gray, sandy clay containing abundant brown and tan phosphate pebbles, but lean brown and tan concentrates.
10 to 15	Gray, sandy clay containing abundant brown and tan small pebbles and abundant brown and tan concentrates.
	Bed Clay (Hawthorne)
15 to 20	Pale yellow bed clay. Contains lean, brown concentrates.

Analyses of hole 2: Summary

Hole	Fraction	Test results		
		T/A	BPL	Insol.
2 (7/8)	plus 14	2704	58.6	15.66
	14/20	669	62.5	11.04
	Conc.	2413	69.2	3.14
	Product	5786	63.5	9.90
	T/A Ft.	723		

HOLE 3—ROY BROWN PROPERTY

Section 31, T. 10 S., R. 22 E. Log by: C. O. Ensign

Feet	*Overburden* (Post-Hawthorne)
0 to ½	Black, sandy top soil.
½ to 1	Gray sand, medium grained.
1 to 3	Tan, water bearing sand, medium grained.
3 to 11½	Gray, water bearing sand containing a trace of white phosphate nodules; at 10 feet quartz sand becomes coarse grained.
	Matrix (Hawthorne)
11½ to 15	Gray, sandy clay containing white phosphate pebbles and white and dark gray concentrates.
15 to 20	Whitish-gray, sandy clay containing brown concentrates and lean soft white concentrates. This stratum is similar to bed clay in appearance.

Feet *Bed Clay* (Hawthorne)

20 to 21½ Pale yellow, calcareous bed clay.

Analyses of hole: Summary

Hole	Fraction	Test results		
		T/A	BPL	Insol.
3 (11½/8½)	plus 14	1032	58.3	17.16
	14/20	565	58.7	17.07
	Conc.	2340	70.0	2.99
	Product	3937	65.3	8.72
	T/A Ft.	463		

HOLE 4—ROY BROWN PROPERTY

Section 31, T. 10 S., R. 22 E. Log by: E. C. Pirkle

Feet *Overburden* (Post-Hawthorne)

0 to 1 Loose, gray, slightly clayey sand.

1 to 2½ Loose, whitish sand with clay content increasing with depth.

2½ to 4 Light gray, clayey sand.

4 to 5 Clayey sand containing pebbles of sandrock.

5 to 5½ Largely sandrock.

Matrix (Hawthorne)

5½ to 8½ Clayey sand with abundant white and gray pebbles and grains of phosphate. Pebble size dominant. Color of clay changes with depth from gray to brown to gray.

8½ to 10½ Sandy, greenish clay with abundant pebbles and grains of brown phosphate. Decrease in pebble and increase in concentrates.

10½ to 14½ Grayish, sandy clay or clayey sand with abundant phosphate pebbles. Brown concentrates.

Bed Clay (Hawthorne)

14½ to 17½ Pale yellow bed clay with occasional pebbles of brown phosphate.

Analyses of hole: Summary

Hole	Fraction	Test results		
		T/A	BPL	Insol.
4 (5½/9)	plus 14	2882	59.2	15.90
	14/20	758	62.9	11.27
	Conc.	1477	69.6	3.08
	Product	5117	62.8	11.51
	T/A Ft.	569		

HOLE 5—ROY BROWN PROPERTY

Section 31, T. 10 S., R. 22 E. Log by: Overburden—C. O. Ensign.

Matrix—E. C. Pirkle

Feet	*Overburden* (Post-Hawthorne)
0 to 1	Medium, gray sand.
1 to 5	Chocolate brown sand grading into cream sandy clay.
5 to 7	Intercalated stiff gray and brown sandy clay.
7 to 18	Stiff, gray, sandy clay with intercalated brown, sandy, clay laminae. At 9 feet sandrock pebbles appear. At 12 feet a trace of white phosphate appears.
	Matrix (Hawthorne)
18 to 21½	Heavy gravel of phosphate pebbles.
21½ to 24½	Light gray, clayey sand containing abundant phosphate particles. A decrease in pebble size and an increase in brown concentrates.
24½ to 33½	Slightly clayey sand with abundant brown concentrates and small pebbles of phosphate.
	Bed Clay (Hawthorne)
33½ to 42½	Pale yellow bed clay. Becomes more gray with depth.

Analyses of hole: Summary

Hole	Fraction	Test results		
		T/A	BPL	Insol.
5 (18/15½)	plus 14	4293	61.2	17.01
	14/20	1109	61.5	13.34
	Conc.	4651	70.2	2.63
	Product	10,053	65.4	9.95
	T/A Ft.	649		

Generalizations Concerning Pebble Phosphate

A number of analyses of phosphate from Alachua County are listed in Appendix "A." From those analyses, from the preceding data concerning phosphate on the property of Mr. Roy Brown and from a general knowledge of the geology of the county, it is believed that all of the phosphate in the zone of concentration at the top of the Hawthorne in the plateau area of Alachua County is low-grade, although in some areas there is a considerable tonnage of phosphate.

The low BPL content results in large part from the high percentage of included material within the pebble. Much of this material is quartz sand.

enriched by replacement of part of the remaining carbonate content of the nodules by phosphate. Underlying limestone would be favorable because it would facilitate the movement of groundwater.

Even though it may be possible that major changes in processing phosphatic sediments may be developed in the future, at the present time the pebble phosphate at the top of the Hawthorne formation in the plateau area of Alachua County is not of sufficiently high grade to be mined. Nor is it believed that the mining will be economically feasible in the near future.

Though it is true that phosphate producers must eventually mine lower grade material, there is a great quantity of low-grade phosphate in the Bone Valley district. Pebble phosphate also is known from Hamilton, Bradford, Clay and other counties (4). The pebble phosphate at the top of the Hawthorne formation in the plateau area of Alachua County adds to the low-grade phosphate reserves of the State of Florida a minimum of between 30 and 50 million tons of phosphate particles that will average better than 50 percent BPL.

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Dec. 1, 1956

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APPENDIX "A"

Phosphate Analyses

1. Sample taken just north of canal at Gainesville Airport.
Hole drilled by hand auger.
Mechanical analyses made by Mr. James Cathcart.
Chemical analyses run by American Cyanamid Company.

Overburden—23 feet
Strata—6½ feet (did not penetrate).

Screen analyses

	Wt. (gms)	Wt. %	Wt. % conc.	Wt. (gms) conc.	Sand	% Wt. conc.	Sand
+6	2180.7	28.4	——		All phosphate		——
6/12	1126.2	14.6	——				——
12/20	887.7	11.6	——		Minor sand		——
20/40	1199.1	15.6	10.8	832.2	366.9	69.4	30.6
40/50	403.3	5.3	2.7	240.7	162.6	51.0	49.0
50/70	403.9	5.3	1.8	134.9	269.0	33.4	66.6
70/100	156.4	2.0	0.4	28.9	127.2	18.5	81.5
100/140	87.1	1.1	0.2	12.8	74.3	14.7	85.3
140/200	27.8	0.4	0.07	4.8	23.0	17.3	82.7
−200	1220.7	15.9	——	Some phosphate grains visible, about 15%			
	7692.9						

	Tonnages (long tons)	(115 pounds/cubic foot)
+6	4128	
6/12	2122	
12/20	1686	54.6% pebble
	7936 (Total pebble, tons per acre)	
20/40	1570	
40/50	392	
50/70	262	15.97% conc.
70/100	58	
100/140	29	
140/200	10	
	2321 (Total concentrate, tons per acre)	

Phosphate = 70.5%; Sand = 13.6%; Slime = 15.9%

Description	*B.P.L.*	*Insol.*
Pebble:		
Plus 6 Mesh	56.15	19.46
Minus 6 Plus 12	59.89	14.62
Minus 12 Plus 20	62.10	12.68
Feed:		
Minus 20 Plus 40	57.14	19.52
Minus 40 Plus 50	38.06	46.35
Minus 50 Plus 70	25.00	64.28
Minus 200 Mesh	12.98	61.48
Concentrate:		
Minus 20 Plus 40	68.89	3.28
Minus 40 Plus 50	69.35	2.51
Minus 50 Plus 70	69.13	3.47
Minus 70 Plus 100	65.16	9.10
Minus 100 Plus 140	57.47	18.53
Minus 140 Plus 200	47.81	31.64

2. NW¼ of NW¼ Section 13, T. 9 S., R. 20 E., Alachua County.
Hole drilled with a Permanco, trailer-mounted, gasoline-driven, power-auger.
Data furnished by American Cyanamid Company.

0–1	Black sandy soil.
1–3	White, loose, medium to fine-grained sand.
3–10	Brown, iron-stained sand, lighter with depth.
10–13	White, loose sand.
13–20	Clayey sand, with beds of gray sandy clay.
20–40	Cream to white, loose to slightly clayey sand; minor brown phosphate becoming more abundant with depth.
40–60	Greenish-gray clayey sand, grading to sandy clay at base. Abundant black phosphate.

Sample A—40–60

Sample No.	+20 Mesh		Insol. pebble	Corrected		T.P.A. conc.	B.P.L. conc.	Insol. conc.	Ratio
	T.P.A. pebble	B.P.L. pebble		T.P.A. feed	B.P.L. feed				
A	2,031	50.06	16.67	24,222	10.27	2,479	61.01	7.39	9.77

3. NE¼ of NW¼ Section 24, T. 9 S., R. 20 E., Alachua County.
Hole drilled with a Permanco, trailer-mounted, gasoline-driven, power-auger.
Data furnished by American Cyanamid Company.

0–3	Black and brown, loose sand.
3–6	White, loose sand.

6–15 Light brown, iron-stained sand (hardpan) grading to tan, loose sand at base.

15–33 Light gray, very slightly clayey sand.

33–40 Light gray sandy clay to clayey sand, with abundant brown pebble phosphate.

40–60 Light gray-green clay with abundant, black fine-grained phosphate.

60–70 As above, but slightly stiffer.

T. D. 70 feet

Sample A—33–40

Sample B—40–60

Sample C—60–70

Sample No.	+20 Mesh		Insol. pebble	Corrected		T.P.A. conc.	B.P.L. conc.	Insol. conc.	Ratio
	T.P.A. pebble	B.P.L. pebble		T.P.A. feed	B.P.L. feed				
A	1,097	58.14	17.91						
	686	61.31	14.33	7,131	18.68	1,602	68.48	3.57	4.45
B	214	57.36	17.78						
	463	55.17	20.15	27,463	11.76				
						4,981	62.97	4.11	6.75
C	1,175	34.52	11.40						
	588	37.04	12.85	6,162	16.15				
	4,223	48.78	15.05	40,756	13.63	6,583	64.31	3.98	6.19

4. SW¼ of SW¼ Section 23, T. 9 S., R. 20 E., Alachua County.

Hole drilled with a Permanco, trailer-mounted, gasoline-driven, power-auger.

Data furnished by American Cyanamid Company.

0–8 Gray, brown, and yellow loose sand.

8–12 Light brown, iron-stained sand (hardpan).

12–18 Light gray, very slightly clayey sand.

18–25 Light buff, fine, loose sand, trace dark fine phosphate.

25–30 Light greenish-gray clayey sand, trace black-white phosphate.

30–37 Greenish-gray, clayey sand, pebble and float phosphate, approximately 10 percent.

37–43 As above, pebble increasing.

43–53 As above, abundant coarse pebble.

53–60 As above, only trace pebble.

Sample A—30–37

Sample B—37–43

Sample C—43–53

Sample No.	+20Mesh		Insol. pebble	Corrected		T.P.A. conc.	B.P.L. conc.	Insol. conc.
	T.P.A. pebble	B.P.L. pebble		T.P.A. feed	B.P.L. feed			
A	1,193	55.80	16.95					
	677	51.98	15.26	7,801	10.07			
B	1,015	53.73	16.86					
	410	48.05	17.82	6,661				
C	1,745	54.60	17.21					
	463	51.87	16.61	8,371	9.53			
	5,503							

5. Center of the NE¼ Section 34, T. 8 S., R. 20 E., Alachua County.

Hole drilled with a Permanco, trailer-mounted, gasoline-driven, power-auger.

Data furnished by American Cyanamid Company.

0–3 Sand, gray, loose.

3–10 Clay, sandy, gray, with blue-green clay lenses?

10–24 Sand, clayey, white to gray (Kaolinitic?) lenses, darker and more clayey toward base.

24–44 Clay, sandy, ("salt and pepper") with black, mostly fine grained phosphate nodules—mines coarse.

44–58.5 Clay, dark gray, with black phosphate, decreasing toward base.

T. D. 58.5′ in hard rock.

Sample A—24–44

Sample B—44–58.5

Sample No.	+20 Mesh		Insol. pebble	Corrected		T.P.A. conc.	B.P.L. conc.	Insol. conc.	Ratio
	T.P.A. pebble	B.P.L. pebble		T.P.A. feed	B.P.L. feed				
A	71	54.38	17.42						
	71	37.93	41.73	10,098	15.10	1,846	68.67	2.56	5.47
B	801	34.24	12.92						
	542	37.49	27.03	12,241	19.80	2,921	65.94	2.24	4.19
	1,485	36.57	19.66	22,339	17.68	4,767	67.00	2.36	4.69

6. SW¼ of NW¼ Section 18, T. 9 S., R. 20 E., Alachua County.

Hole drilled with a Permanco, trailer-mounted, gasoline-driven, power-auger.

Data furnished by American Cyanamid Company.

0–1 Black soil.

1–3 Sand, clayey to loose, gray to tan.

3–18 Sand, clayey, gray.
18–24 Clay, sandy, light gray to white, abundant coarse and fine phosphate.
24–30 Clay, yellow-brown, sticky, abundant pebble phosphate.
30–45 Clay, khaki, sandy, flotation size phosphate.
45–60 Clay, buff to tan, bluish, with phosphate grains.

Sample A—18–24 feet
Sample B—24–30
Sample C—30–45
Sample D—45–60

Sample No.	+20 Mesh		Insol. pebble	Corrected		T.P.A. conc.	B.P.L. conc.	Insol. conc.	Ratio
	T.P.A. pebble	B.P.L. pebble		T.P.A. feed	B.P.L. feed				
A	1,069	44.90	9.80						
	470	43.92	7.21	3,847	12.08	561	57.75	3.67	6.86
B	641	50.58	10.04						
	278	50.47	8.40	5,514	6.16				
C	196	47.20	16.47						
	142	41.52	23.83	9,617	9.68				
D	142	47.31	17.20						
	89	45.67	23.39	11,078	8.37				
	3,027	46.59	11.16	30,056	8.86	2,952	62.58	4.68	10.18

7. Analyses of a 13 pound sample collected at an exposure on south side of dirt road, just west of a tributary of Lochloosa Creek (Sec. 25, T. 10 S., R. 21 E.).
Analyses furnished by American Metal Company, Limited.
Chemical analyses run by Thornton and Company of Tampa, Florida.
Weight of Matrix (wet) 13.00 lbs.
Weight of $-\frac{1}{2}$ plus 14 phosphate (dry) 3.25 lbs.

	Wet screening—$-\frac{1}{2}$ plus 14	Flotation—14 plus 150		Heads	Slime
		Concentrate	Tailings		
Tons per Acre Foot	576	224	587	811	
Phosphoric Acid (P_2O_5)	24.32%	30.26%	3.20%	10.68%	19.30%
B.P.L.	53.14%	66.12%	7.00%	23.34%	42.17%
Iron and Alum. Oxides	6.41%	5.43%	——	——	
Insoluble	23.76%	4.00%	90.11%	66.30%	

FLOTATION FEED

Ratio: Dry feed to dry recovered phosphate, flotation -14 plus 150 *3.62* to 1.

Composition: Dry Concentrate 27.62%
Dry Tails 72.38%

8. Analyses of a 35 pound sample collected from top of Hawthorne formation at the Devil's Mill Hopper, Alachua County (Sec. 15, T. 9 S., R. 19 E.).

Data available through the courtesy of the American Metal Company, Limited.

Chemical analyses run by Thornton and Company of Tampa, Florida.

Weight of Martix (wet) 35 lbs.

Weight of $-\frac{1}{2}$ plus 14 phosphate (dry) 8.62 lbs.

	Wet screening—$-\frac{1}{2}$ plus 14	Flotation—14 plus 150		Heads	Slime
		Concentrate	Tailings		
Tons per Acre Foot	543	182	666	848	
Phosphoric Acid (P_2O_5)	26.86%	31.06%	3.20%	9.19%	7.87%
B.P.L.	58.70%	67.86%	7.00%	20.07%	17.19%
Iron and Alum. Oxide	5.10%	4.72%			
Insoluble	14.62%	4.00%	88.08%	70.02%	

FLOTATION FEED

Ratio: Dry feed to dry recovered phosphate, flotation -14 plus 150 *4.66* to 1.

Composition: Dry Concentrate 21.46%

Dry Tails 78.54%

SOME SUGGESTIONS CONCERNING THE SEQUENCE OF CERTAIN ORE MINERALS

H. E. McKINSTRY AND G. C. KENNEDY

ABSTRACT

Phase diagrams for the ore minerals in the systems Cu-Fe-S, Fe-O-S, Cu-As-S, Pb-As-S and Pb-Sb-S are postulated, based on the observed sequence in various mining districts.

These diagrams strongly suggest the sequence of phases that appear in each of these systems and can be readily explained by assuming an increase in chemical potential of sulfur in the fluid mineralizing phase relative to that of the solid phases during the period when final adjustments in relations among the solid phases is taking place. The sequence of phases at a point in a vein and the sequence of introduction of components into a vein are not necessarily the same.

INTRODUCTION

Few attempts have been made to apply the Gibbs phase rule to sulfide mineral deposits, perhaps largely because sulfide mineral assemblages are so obviously disequilibrium assemblages. However disequilibrium assemblages of vein materials are most marked when examined on a gross scale, i.e. an entire vein or portions of a vein. Sufficiently small volumes of an ore deposit in many cases show apparent equilibrium assemblages of minerals. Examination of these small units of a mineral deposit, small even in terms of the scale of a microscope field, yields a picture of a succession of equilibrium conditions and it is the direction of change of this succession of equilibrium conditions that we wish to examine.

The Gibbs phase rule states that the maximum number of phases in a system equals the number of components plus two minus the number of degrees of freedom

$$p = c + 2 - f.$$

Goldschmidt, recognizing that most mineral assemblages must have formed over a considerable range of temperatures and pressures, noted that the number of degrees of freedom must be at least two, pressure and temperature. Thus he formulated the mineralogical phase rule

$$p = c.$$

Korzhinsky (8, 9) has discussed the application of the phase rule to open systems. Korzhinsky's rule states that the number of phases cannot exceed the number of fixed components. Thus, the various three-component systems we consider in this paper always contain sulfur as one of the components. Insofar as veins may be considered open systems with sulfur present in fluid

phase, the number of possible solid phases is reduced by one and only two mineral phases may be present in equilibrium. The triangular diagrams we present in this paper are therefore strictly applicable only to completely condensed systems, and show three possible solid phases in equilibrium. In open systems such as veins however, only two of these phases may be in equilibrium, with pressure and temperature varying and a sulfur rich fluid phase present. Thus we may assume that in typical cases our systems are always in disequilibrium, one of three minerals always being replaced by another.

The extent to which most sulfide deposits, on a gross scale, represent disequilibrium assemblages is immediately apparent. For example only three solid phases can be present in equilibrium in the condensed system Cu-Fe-S if pressure and temperature are variables, yet mineral assemblages that contain pyrite, marcasite, pyrrhotite, digenite, chalcocite, covellite, bornite, chalcopyrite, and others, are known; these assemblages have as many as five more phases than should be present in equilibrium.

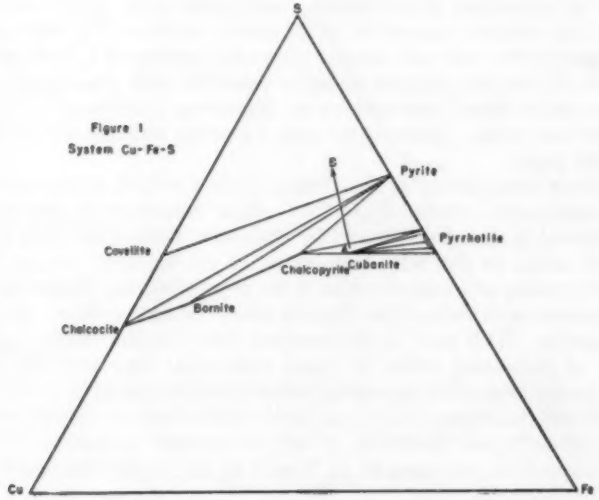
Although the number of solid phases in equilibrium at any given temperature, pressure, and composition in a three-component system is small, the identity of the solid phases may change in response to changes in the variables: temperature, pressure, and composition. Thus, during formation of a sulfide deposit, earlier-formed minerals are constantly being altered toward new compositions, i.e. replaced, in response to changes in the variables of the system. The replacement rarely, if ever, is complete and thus an ore deposit mirrors a history of changing conditions of equilibrium. The sequence of phases as indicated in hand specimens and under the microscope gives some indication of the direction of changing equilibrium conditions. It is these changing equilibrium conditions that we wish to examine.

Many observations have been made about the "usual sequence" of sulfide minerals. Gilbert (5) has observed that minerals appear in decreasing order of their relative hardness. Schürmann (11) noted a sequence of replacement among sulfides which was later shown to be approximately the inverse order of their solubility in water at room temperature. Bandy (1) has noted that the "normal" or "ideal" sequence is in approximate order of increasing proportions of cations to anions. Some aspects of sulfide sequence may be explored by aid of ternary diagrams of various condensed sulfide systems.

THE SYSTEM Cu-Fe-S

A great amount of detailed mineralogical information is available about relations between solid phases in the system Cu-Fe-S. Sales and Meyer (1949) postulate that at Butte ascending solutions react with iron-bearing minerals in the wall rock to form pyrite. Solutions thus depleted in sulfur then deposit chalcopyrite and bornite. Once the iron-bearing wall-rock minerals are converted to pyrite, the early chalcopyrite-bornite assemblage is replaced by the assemblage chalcocite and pyrite, which for a given copper-iron ratio is more sulfur-rich. The compositions of various solid phases in the condensed system Cu-Fe-S are plotted in Figure 1. We can draw various tie lines and erect a postulated ternary phase diagram.

Let us postulate that during the course of mineral deposition the partial pressure of sulfur increases, or some change takes place so that the relative chemical potential of sulfur at any one point in a vein increased with time. The expected mineralogical changes in the condensed system can be seen by the course of the arrow, Figure 1, from A to B. The assemblage stable at point A is cubanite, pyrrhotite, and chalcopyrite. As the sulfur potential increases along the path AB, the triangular field where pyrite, pyrrhotite and chalcopyrite are the stable phases is entered and cubanite disappears. With further change toward the S corner, the triangular field of pyrite, bornite, and chalcopyrite is entered and pyrrhotite disappears. The next phase to disappear is chalcopyrite as chalcocite appears. Bornite then disappears as covellite ap-



pears and even chalcocite will disappear if relative sulfur chemical potential is sufficiently high and sulfur content of the condensed system increases. We can now arrange the sulfides in the Cu-Fe-S system in a sequence based on the assumption of steadily increasing relative chemical potential of sulfur during mineral deposition. From early to late, stable phase assemblages are:

cubanite,* pyrrhotite, chalcopyrite
pyrite, pyrrhotite, chalcopyrite
bornite, pyrite, chalcopyrite
chalcocite, bornite, pyrite
covellite, chalcocite, pyrite

* Cubanite commonly, if not invariably, occurs intergrown with either chalcopyrite or pyrrhotite, presumably representing unmixing of a solid solution stable above 400 or 500°. The problem has been discussed by Borchert, Edwards and others. In ores presumably formed at lower temperatures, pyrrhotite and chalcopyrite occur together but cubanite is usually lacking.

The last three groups represent the sequence found by Sales and Meyer at Butte; this is also the sequence of phases reported by mineragraphers for a large majority of ore deposits. Not all the groups of stable phases, of course, may be present in any one vein or mine. Pyrrhotite and cubanite are absent at Butte, and in many deposits the later stages, chalcocite and covellite, are not represented in the hypogene mineral suite. In many of the deposits, moreover, the evidence of extraction of sulfur by wall rock minerals is lacking, or at least has not been reported. We would like to suggest that this aspect of the Sales and Meyer story of Butte may not necessarily be an integral part of the general genetic picture. Characteristically, the sequence of phases that appear in the system Cu-Fe-S is one most readily explained by assuming increase with time of the relative chemical potential of sulfur. Early extraction of sulfur by conversion of iron-bearing wall minerals to pyrite will certainly permit a later relative increase in sulfur concentration of the solutions as the iron minerals in the wall rock become completely converted to sulfides. However, a steady relative increase of sulfur potential with time appears to take place even when there is no evidence of decreasing fixations of sulfur by the iron of the wall rocks. Reasons for such a possible increase will be discussed later in this paper.

The above examination of the phases in the Cu-Fe-S system points up a possibly unexpected relationship. The major sequence of phases, chalcopyrite followed by bornite, followed by chalcocite, takes place with increasing amount of sulfur in the bulk composition of all the solid phases but with actually decreasing amounts of sulfur in the copper bearing phases, for chalcopyrite contains more sulfur than bornite which in turn contains more sulfur than chalcocite. This part of the sequence thus fits both with Bandy's observation of decreasing sulfur to metal ratio with time and our thesis of sequence owing to steadily increasing sulfur chemical potential in the mineralizing fluids and consequent increase of sulfur with time in the condensed phases. Covellite, cubanite and pyrrhotite would be apparent exceptions in Bandy's scheme of sequence, but seem to fit in well as far as our hypothetical phase diagram is concerned.

Our hypothetical phase diagram also explains Gilbert's generalization that bornite and pyrrhotite are incompatible. There are in the world many pyrrhotite-chalcopyrite deposits, such as Noranda (Quebec), Sherritt Gordon (Manitoba), Ducktown (Tennessee) and South Strafford (Vermont). In all of these bornite is absent or a rarity. Likewise hypogene chalcocite is virtually if not completely absent. On the other hand, deposits containing bornite, such as Butte and most of the porphyry copper deposits, contain no pyrrhotite.

THE SYSTEM Fe-O-S

Hypogene solid phases in the system Fe-O-S are magnetite, hematite, pyrite, and pyrrhotite. Their genetic relations have been discussed extensively by Gilbert (4, 6) and by numerous other writers.

Hydrothermal magnetite and hematite in appreciable quantity are found almost exclusively in high temperature limestone environments. Probably the

formation of metasomatic calcium silicates frees CO_2, which at the relatively high temperature of these deposits, partially dissociates and oxidizes the iron in the hydrothermal solutions. The reactions are summarized by the equations:

$$2\ CaCO_3 + SiO_2 = Ca_2SiO_4 + 2\ CO_2$$
$$2\ CO_2 = 2\ CO + O_2$$
$$O_2 + 6\ FeO = 2\ Fe_3O_4$$

Magnetite, Fe_3O_4, is extremely insoluble, and will precipitate readily so that the various reactions continue to run. The CO escapes upward with the partially spent hydrothermal solution.

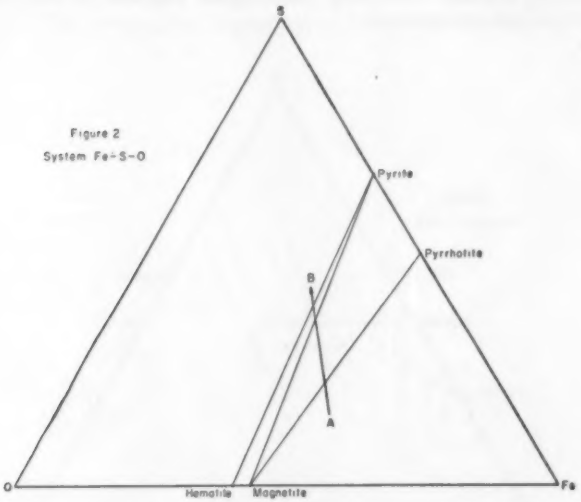


Figure 2
System Fe-S-O

The relationships between the phases in the system Fe-O-S suggest that in the vast majority of cases early silicates are followed by magnetite with pyrrhotite, followed by later hematite and pyrite. In this system, hematite and pyrrhotite seem to be incompatible species. The postulated diagram, Figure 2, appears to explain fairly well the observed relationships. Again, the sequence of phases indicates a steadily increasing amount of sulfur in the condensed system. Our phase diagram suggests that the stable groups are pyrite-magnetite-pyrrhotite and hematite-pyrite-magnetite.

THE SYSTEM Cu-As-S

The solid phases in the system Cu-As-S are shown in Figure 3. The relations between enargite and tennantite have been studied in numerous ore deposits as well as experimentally.

Sales and Meyer have shown that at Butte, tennantite is followed by

enargite at about the time chalcopyrite and bornite are followed by chalcocite and pyrite. Enargite is displaced from tennantite almost directly toward the sulfur corner of the triangular diagram and Sales and Meyer have interpreted the shift from tennantite to enargite as a result of increasing sulfur concentration in the solution. Gaines (3) has shown experimentally that enargite crystallizes from hydrothermal solutions at higher partial pressures of sulfur, and tennantite forms from the same solutions at lower partial pressures of sulfur.

On the As-S side of the three component system, the phases realgar and orpiment are of interest. Here also, orpiment seems to be the later of the two phases. It occurs in many cases as veins cutting realgar and as late alteration crusts on realgar. In many deposits, the relations of these two phases are, however, not unequivocal.

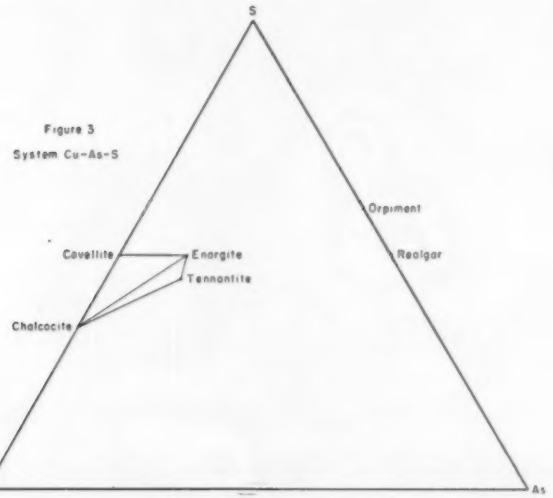


Figure 3
System Cu-As-S

THE SYSTEM Pb-As-S

The sequence of phases in the systems discussed so far appears to be explainable on the assumption that the volatile component, S, increases in relative chemical potential with time at a given point in a vein, thus causing relative amounts of sulfur in the various condensed systems to increase.

It is of interest, therefore, to examine the more volatile compounds of sulfur whose behavior might be expected to parallel that of sulfur. These compounds are As_2S_3 and Sb_2S_3.

With the exception of realgar and native arsenic, the compositions of all the minerals in the system Pb-As-S lie on a straight line between that of galena and that of orpiment. All the minerals are rare and many of them are re-

ported only at Binnenthal in Switzerland. The phases reported in this system are:

	PbS	As_2S_3
Orpiment	0	1
Sartorite	1	1
Liveingite	5	4
Baumhauerite	4	3
Rathite	3	2
Dufrenoysite	2	1
Guitermanite	3	1
Jordanite	4	1
Gratonite	9	2
Galena	1	0

The compositions of these minerals are plotted on the triangular diagram in Figure 4. The sequence of deposition at Binnenthal, according to Boder

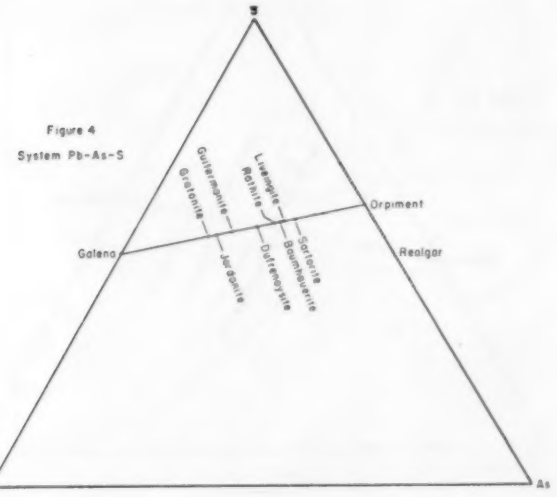


Figure 4
System Pb-As-S

(2), is in order of progressive increase in the As_2S_3 content. Jordanite is replaced by dufrenoysite and by baumhauerite; rathite by baumhauerite, by sartorite and by realgar. Galena in this district is rare and is commonly associated with jordanite. The sequence of phases can, of course, be readily explained by assuming that the arsenic behaves in a manner somewhat similar to sulfur in that its relative chemical potential increases also with time at a given point in a vein.

THE SYSTEM Pb-Sb-S

A large number of phases occur in the system Pb-Sb-S. All of the compositions except that of native antimony, fall on a straight line between that

of galena and stibnite and are shown in Figure 5. The various phases are:

	PbS	Sb_2S_3
Galena	1	0
Boulangerite	5	2
Semseyite	9	4
Plagionite	5	4
Zinkenite	1	1
Fuloppite	3	4
Stibnite	0	1

The detailed genetic relations of these minerals are not known. However, in several localities boulangerite follows galena and is followed by stibnite.

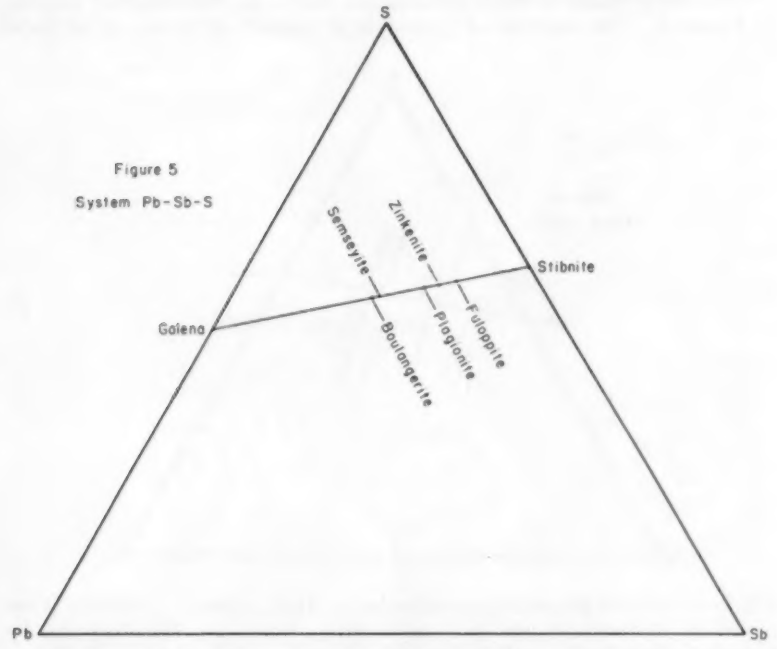


Figure 5

System Pb-Sb-S

Available evidence strongly suggests thus that the relative chemical potential of Sb_2S_3 in the ore-forming fluid increases with time as does that of As_2S_3 and S.

DISSOCIATION OF SOLID PHASES

In summary, then, the three-component systems examined to date show a rather striking trend. The relative chemical potential of the more volatile component of the solid phases apparently increases in the ore-forming fluid with time during ore deposition at any fixed point in a vein and successively

later phase assemblages are enriched more and more in sulfur, antimony sulfide, or arsenic sulfide as the case may be.

We perhaps may clarify these relations by considering the equilibrium between a volatile and a solid. Let us take, for example, the compounds CuS and Cu_2S. The relation between dissociation pressure and temperature for these two phases is shown in Figure 6. Curve A in Figure 6 is the dissociation sulfur vapor pressure of CuS. Curve B is the dissociation sulfur vapor pressure of Cu_2S. The graph shows the partial pressure of sulfur vapor plotted versus temperature. The stability fields of chalcocite, covellite and metallic copper are shown. Along curve A, the chemical potential of sulfur in

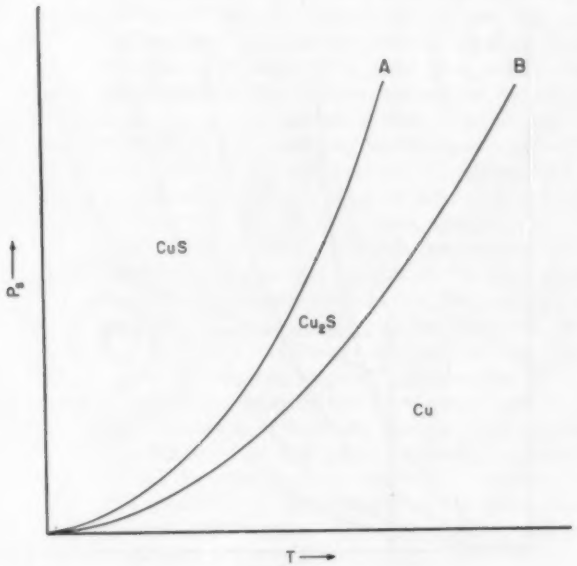


Figure 6

the vapor phase plus the chemical potential of chalcocite is the same as that of covellite, whereas along curve B, metallic copper and sulfur vapor are in equilibrium with chalcocite. Were there copper sulfides containing more sulfur than covellite, their boundary curves would, of course, be farther to the left than that of covellite diagram. As the relative sulfur chemical potential is raised, we progress from the field where metallic copper is stable to the field where chalcocite is stable and on to the field where covellite is stable.

The equations of the dissociation curves A and B are simple. They are given by the Clausius-Clapeyron equation $dp/dt = \Delta H/T\Delta V$. In the region of modest to high temperatures and relatively low sulfur-vapor pressures, the ideal gas law may be substituted. Neglecting the volume of the solid phases

and substituting $V = RT/p$, we have

$$dp/dt = p\Delta H/RT^2$$
$$\ln p = \Delta H/RT + C. \quad \text{by integration}$$

In this equation ΔH is, of course, the heat of dissociation and R is the gas constant. Thus the partial pressure of sulfur in equilibrium with a sulfide reaches zero only at a temperature of absolute zero on the Kelvin scale.

The sequence of phases in the three-component systems discussed earlier in this paper suggested strongly that each successive phase or phase assemblage was steadily enriched in the more volatile component. The history of the

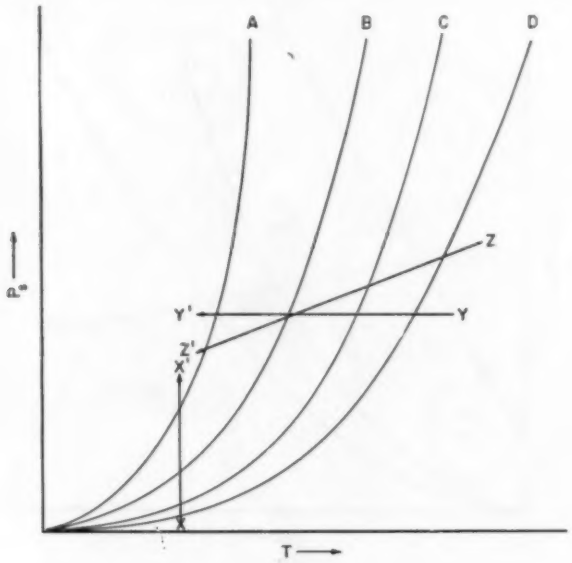


Figure 7

ore-forming fluid may thus be indicated on a PT plane such as Figure 7. In Figure 7, the curves A, B, C, and D represent curves of the dissociation pressures of various solid phases or phase assemblages. The partial pressure of the volatile component, S, As_2S_3 or Sb_2S_3 in the systems earlier described, is plotted versus temperature. It is immediately apparent that the transition from phase D to C to B to A, in equilibrium with the ore-forming fluid, can take place with the composition, temperature and partial pressure of sulfur in the fluid changing along a great variety of paths. Three possible paths, all with the same sequence of phases, are shown in Figure 7. These paths are indicated by XX′, and YY′ and ZZ′.

Thus, the path of the ore fluid might be XX′, a path where temperature

remains constant or rises and the partial pressure of the volatile component of the ore mineral increases with time. This is the path postulated by Sales and Meyer for Butte. However, alternative paths, such as YY′ or ZZ′, will give the same phase assemblages and sequence of phases. In path YY′, partial pressure of the volatile remains constant and temperature steadily declines. In the case ZZ′, partial pressure of the volatile component declines as temperature declines.

In all three cases, XX′, YY′, ZZ′, the volatile component will be extracted from the system due to reactions between earlier solid phases and the ore fluid as each of the curves D, C, B, or A is crossed. Thus, the path of the solution will tend to be offset down slope as each boundary curve is crossed.

It is apparent from Figure 7 that the relations in the three-component systems discussed in this paper lend neither support nor do they disprove the thesis that an apparent mineral sequence at a point in a vein is established during an ascending temperature scale. Indeed, the path of the ore fluid that seems most reasonable to the present author is that of ZZ′ where declining temperature goes hand in hand with declining sulfur partial pressure. This may well put the final imprint on the ore mineral assemblage and give the sequence we observe at any one point. It must be kept clearly in mind that the sequence of phases that we observe in a hand specimen or under the microscope is not necessarily the sequence in which the components were introduced, but rather represents in part the imprint of the final stages of readjustment of the phases as temperature declines and the partial pressure of the various volatile components in equilibrium with the phases decreases. In this respect the behavior of silicates cannot be contrasted too sharply with the behavior of sulfides. Solid diffusion in magmatic silicates is sufficiently slow to be almost non-existent and late stage adjustments among silicate phases is in general trival, though formation of hydrates completely analogous to the reactions among sulfides discussed in this paper is locally important. Solid diffusion in the sulfides, on the other hand, is extremely important and takes place most readily. All workers who have heated sulfide assemblages under experimental conditions can attest to this. Thus, the sequence of phases observed among sulfides represents the relations finally frozen into the mineral assemblage and may have no particularly close bearing on the order of introduction of the components to a given point in the vein. For these reasons the sequence at any one point in a vein system might be expected to be reasonably similar to the succession of zones upward and outward along a vein away from a center of deposition, although the quantities of the phases would be expected to range widely.

AUTHORSHIP AND ACKNOWLEDGMENTS

The suggested phase relationships are based largely on diagrams prepared by McKinstry in 1952; since then similar diagrams for these and other systems have been prepared by students in the Laboratory of Mining Geology, Harvard University. The discussion of their significance in terms of physical chemistry is largely by Kennedy.

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HARVARD UNIVERSITY,
CAMBRIDGE, MASS.,
Jan. 3, 1957

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AN X-RAY MINERALOGICAL STUDY OF SOME BRITISH GUIANA BAUXITE DEPOSITS[1]

G. W. BRINDLEY AND WILLARD H. SUTTON

ABSTRACT

Semi-quantitative mineralogical analyses have been carried out by X-ray diffraction methods on samples taken at 2-foot intervals through the bauxite deposits at four localities in British Guiana. The variation of the gibbsite-kaolinite content, the prevalence of anatase, and the variation in the crystallinity of the kaolinite, are discussed.

A REPORT on "The Bauxite Resources of British Guiana" compiled by D. W. Bishopp has been re-issued in revised form by E. R. Pollard and C. N. Barron (1). In an appendix to this Report, results are given of X-ray analyses by one of us (G.W.B.) of a number of bauxite samples from this area. The specimens were made available by the Director of the Geological Survey, Mr. G. M. Stockley, and were chosen with a view to covering some of the more obvious variations in the bauxite and associated clay deposits. These analyses clarified some of the previous uncertainties regarding mineral content; for example, on p. 60 of the Report the authors describe a "porous ore" which is "grey, with pumice-like texture" with enclosed fragments of "pink ore" and make the comment "surprisingly, X-ray analysis showed both samples . . . to be essentially kaolinite." Material which had previously been classified as halloysite was shown to be kaolinite, and in fact halloysite was not identified in any of the specimens examined with X-rays. On the other hand, kaolinite was found having various degrees of crystalline perfection, as judged from the X-ray data. These analyses, however, did not present an overall picture of the mineralogy at any one locality.

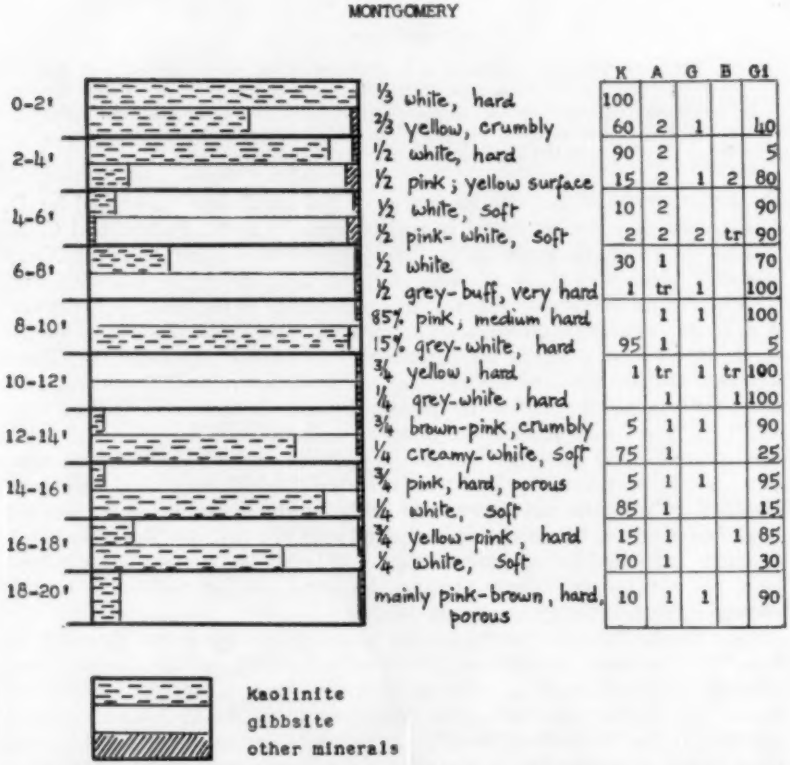
The results described in the present paper are for specimens provided by Mr. W. K. Gummer, Aluminium Laboratories Limited, Arvida, Quebec, from the following localities all of which are described in the Report by Pollard and Barron (1) on the pages indicated: Montgomery (p. 81–85), Nieu Haarden (p. 86), Maria Elizabeth (p. 86–87), and Warababaru (p. 90–91). The first three sites lie close together in the valley of the Demerara River about 60 miles south of Georgetown, and the fourth is on the Ituni River about 90 miles south of Georgetown.

The samples were collected at 2-foot intervals through the bauxite ore body and were supplied in cans with tightly fitting lids so that many were still moist when opened for X-ray analysis. The samples had been crushed to small pebble size, and contained a considerable proportion of finer material. We have no means of judging how representative the samples are of the level from which they were taken. They have been examined principally with the object

[1] Contribution No. 56–26 from The Pennsylvania State University, University Park, Pa.

of determining the kind and proportion of the minerals present and their variation through the four deposits.

The field descriptions of bauxite deposits in British Guiana are usually as follows (1, p. 83): "Hard, bauxite clay; hard grey siliceous ore; hard, grey ore; hard, brown ore; hard, light cream ore; light brown ore; soft light brown ore; soft brown bauxitic clay." These descriptions apply to various deposits



	K	A	G	B	Gi
⅓ white, hard	100				
⅔ yellow, crumbly	60	2	1		40
½ white, hard	90	2			5
½ pink; yellow surface	15	2	1	2	80
½ white, soft	10	2			90
½ pink-white, soft	2	2	2	tr	90
½ white	30	1			70
½ grey-buff, very hard	1	tr	1		100
85% pink, medium hard		1	1		100
15% grey-white, hard	95	1			5
¾ yellow, hard	1	tr	1	tr	100
¼ grey-white, hard		1		1	100
¾ brown-pink, crumbly	5	1	1		90
¼ creamy-white, soft	75	1			25
¾ pink, hard, porous	5	1	1		95
¼ white, soft	85	1			15
¾ yellow-pink, hard	15	1		1	85
¼ white, soft	70	1			30
mainly pink-brown, hard, porous	10	1	1		90

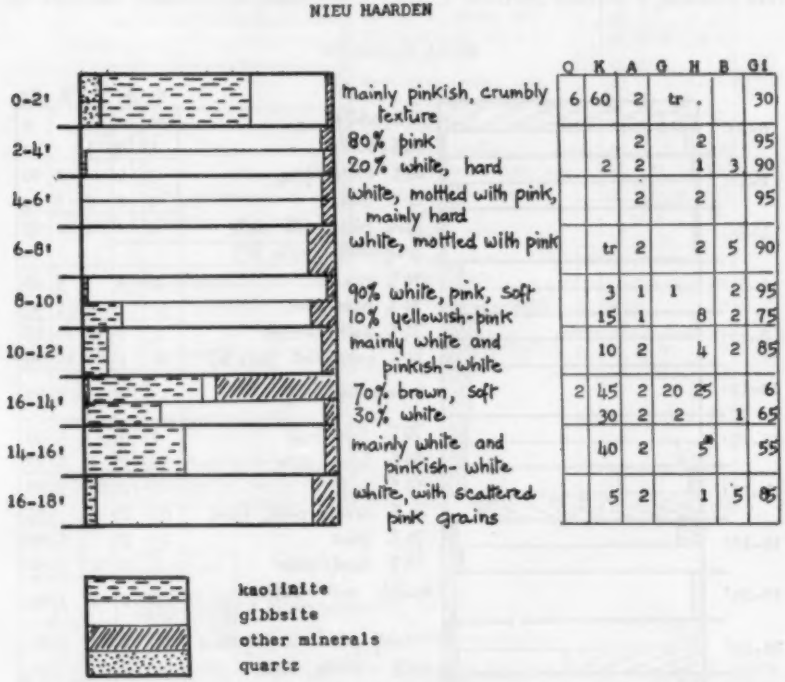
FIG. 1. Montgomery deposit. From 18–20 feet white fragments occur which are about 95 percent kaolinite, 5 percent gibbsite. Percentage mineral composition is indicated in columns K (kaolinite), A (anatase), G (goethite), B (boehmite), Gi (gibbsite).

at the Montgomery Mine. They give virtually no mineralogical information but raise interesting questions as to whether any correlation exists between color, gross texture and mineral content. The present study was aimed principally at answering such questions so far as they can be answered from X-ray diffraction data. Without doubt, more information could be obtained

by additional techniques, especially thin section optical examination and chemical analysis of selected fractions; this however, has not been feasible in the present work.

EXPERIMENTAL DETAILS

X-ray examination has been carried out using a Philips Norelco high-angle X-ray diffractometer mainly with CuKα radiation over the angular



	Q	K	A	G	H	B	Gi
0–2' mainly pinkish, crumbly texture	6	60	2	tr	.		30
2–4' 80% pink			2		2		95
2–4' 20% white, hard		2	2		1	3	90
4–6' white, mottled with pink, mainly hard			2		2		95
6–8' white, mottled with pink		tr	2		2	5	90
8–10' 90% white, pink, soft		3	1	1		2	95
8–10' 10% yellowish-pink		15	1		8	2	75
10–12' mainly white and pinkish-white		10	2		4	2	85
14–16' 70% brown, soft	2	45	2	20	25		6
14–16' 30% white		30	2	2		1	65
16–18' mainly white and pinkish-white		40	2		5*		55
16–18' white, with scattered pink grains		5	2		1	5	85

FIG. 2. Nieu Haarden deposit. Percentage mineral composition is indicated in columns Q (quartz), K (kaolinite), A (anatase), G (goethite), H (hematite), B (boehmite), Gi (gibbsite). 0–2 feet contains white fragments, 80 percent gibbsite. 6–8 feet contains soft brown material, 60 percent kaolinite, 30 percent gibbsite. 8–10 feet contains fragments 50 percent hematite, 40 percent gibbsite, 5 percent kaolinite, 5 percent quartz. 12–14 feet contains fragments 65 percent gibbsite, 30 percent kaolinite.

* Signifies a variable hematite content.

range $2\theta = 2°$ to 70°. Specimens have been lightly ground and mounted in shallow cavities in glass plates. Semi-quantitative analyses have been made by comparison with data for standard mixtures. The principal minerals are gibbsite, $Al(OH)_3$, and kaolinite, $Al_2(Si_2O_5)(OH)_4$. Minor minerals, gen-

erally 5 percent or less by weight, are anatase TiO_2, boehmite AlO(OH), goethite FeO(OH), hematite α-Fe_2O_3, and very rarely quartz and mica. Diffraction traces were prepared of mixtures of gibbsite and kaolinite in the ratios 3 : 1, 1 : 1, and 1 : 3 and of mixtures of the other minerals with gibbsite, using smaller percentages, 1, 5, 10, and 20 percent. This method of estimating mineral content provides sufficient accuracy for the present purpose. An analysis given, for example, as 80 percent gibbsite, 15 percent kaolinite, 2 percent anatase, 1 percent goethite, 2 percent boehmite, is probably accurate to

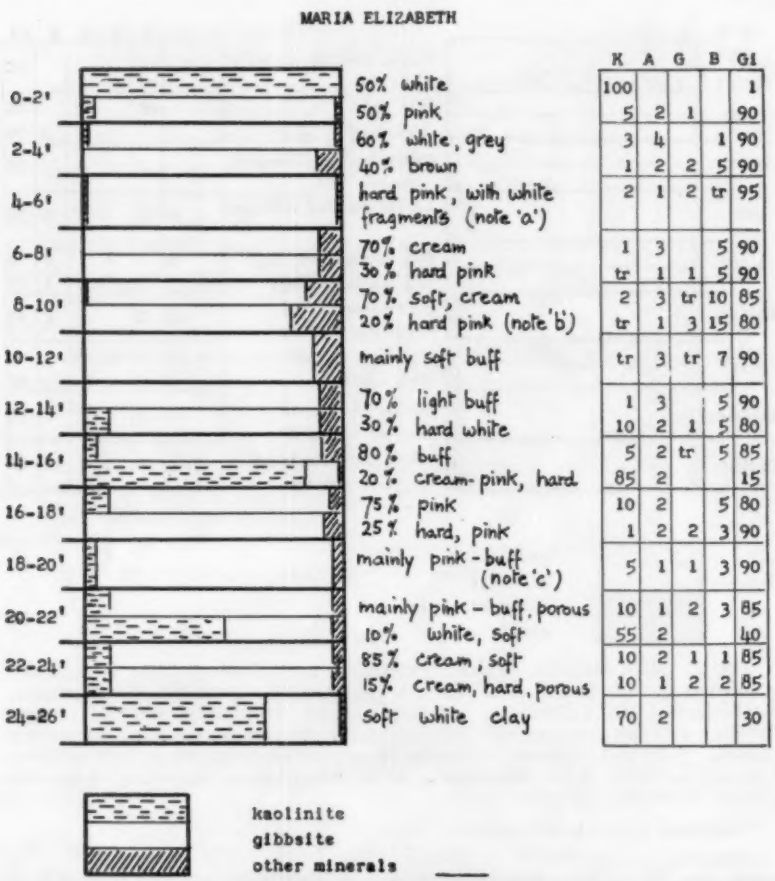

MARIA ELIZABETH
K A G B Gi
0-2'
50% white 100 1
50% pink 5 2 1 90
2-4'
60% white, grey 3 4 1 90
40% brown 1 2 2 5 90
4-6'
hard pink, with white fragments (note 'a') 2 1 2 tr 95
6-8'
70% cream 1 3 5 90
30% hard pink tr 1 1 5 90
8-10'
70% soft, cream 2 3 tr 10 85
20% hard pink (note 'b') tr 1 3 15 80
10-12'
mainly soft buff tr 3 tr 7 90
12-14'
70% light buff 1 3 5 90
30% hard white 10 2 1 5 80
14-16'
80% buff 5 2 tr 5 85
20% cream-pink, hard 85 2 15
16-18'
75% pink 10 2 5 80
25% hard, pink 1 2 2 3 90
18-20'
mainly pink-buff (note 'c') 5 1 1 3 90
20-22'
mainly pink-buff, porous 10 1 2 3 85
10% white, soft 55 2 40
22-24'
85% cream, soft 10 2 1 1 85
15% cream, hard, porous 10 1 2 2 85
24-26'
soft white clay 70 2 30
kaolinite
gibbsite
other minerals

FIG. 3. Maria Elizabeth deposit. (a) White fragments occur of almost pure kaolinite. (b) White segregations occur of 80 percent gibbsite, 20 percent boehmite. (c) Small amount of almost pure, soft white kaolinite. Mineral content is indicated as in Fig. 2.

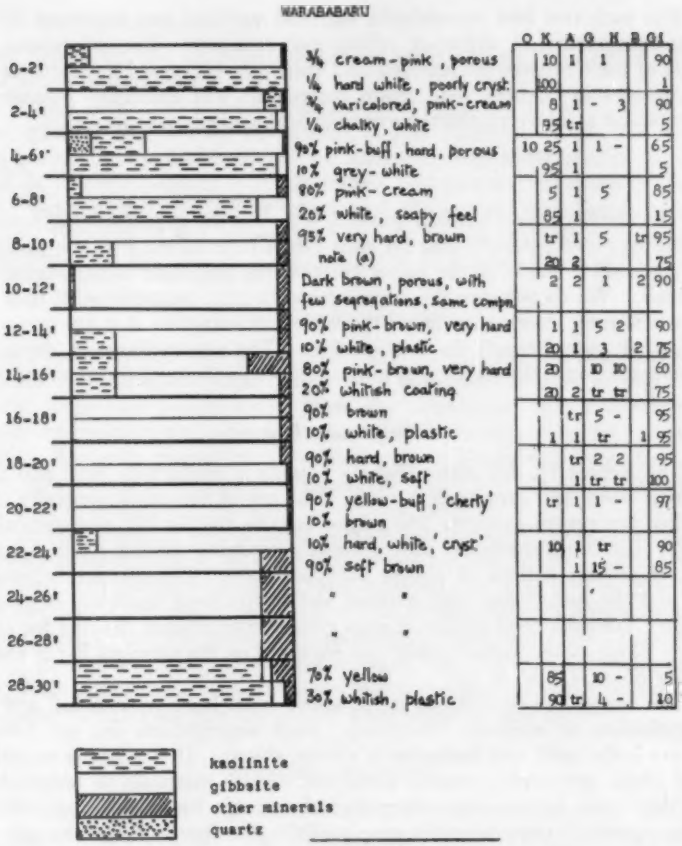

WARABABARU
O K A G K B Gi
0-2'
¾ cream-pink, porous 10 1 1 90
¼ hard white, poorly cryst 100 1
2-4'
¾ varicolored, pink-cream 8 1 - 3 90
¼ chalky, white 95 tr 5
4-6'
90% pink-buff, hard, porous 10 25 1 1 - 65
10% grey-white 95 1 5
6-8'
80% pink-cream 5 1 5 85
20% white, soapy feel 85 1 15
8-10'
95% very hard, brown tr 1 5 tr 95
note (a) 20 2 75
10-12'
Dark brown, porous, with 2 2 1 2 90
few segregations, same compn
12-14'
90% pink-brown, very hard 1 1 5 2 90
10% white, plastic 20 1 3 2 75
14-16'
80% pink-brown, very hard 20 10 10 60
20% whitish coating 20 2 tr tr 75
16-18'
90% brown tr 5 - 95
10% white, plastic 1 1 tr 1 95
18-20'
90% hard, brown tr 2 2 95
10% white, soft 1 tr tr 100
20-22'
90% yellow-buff, 'cherty' tr 1 1 - 97
10% brown
22-24'
10% hard, white, 'cryst' 10 1 tr 90
90% soft brown 1 15 - 85
24-26'
26-28'
28-30'
70% yellow 85 10 - 5
30% whitish, plastic 90 tr 4 - 10
kaolinite
gibbsite
other minerals
quartz

FIG. 4. Warababaru deposit. The nature of the iron oxide may be in doubt; the estimated percentage is then placed midway between the goethite and hematite columns. Otherwise, mineral content is indicated as in Fig. 2. (a) About 5 percent of white material occurs containing about 20 percent kaolinite, 10 percent mica. This is the only case in which mica was observed.

about ± 8 percent for the gibbsite, ± 3 percent for the kaolinite, and ± 0.5 percent for the anatase, goethite and boehmite. Anatase is recognized by one reflection at $d = 3.51$ Å which is adjacent to a strong kaolinite reflection at $d = 3.57$ Å. To verify the presence of anatase, a specimen was treated with warm HCl to remove gibbsite and heated to 600° C to destroy the kaolinite; the full anatase pattern was then clearly seen. The occurrence of anatase rather than rutile has been discussed previously by Brindley and Robinson (1948) in connection with a number of fireclay deposits.

For each two foot interval, the material supplied was separated by hand into components of different colors and textures. Eye-estimations were made of their relative proportions and these are expressed as fractions or as percentages in Figures 1–4. Each component was examined separately by X-rays and a semi-quantitative mineralogical analysis was made.

RESULTS

The results are set out in Figures 1–4 and in the accompanying notes. It should be noted carefully that for each 2-foot interval we give the percentage or fractional estimate of the major components and their mineralogical composition. We do not give the overall mineralogical composition at each level, since it is more informative to see the variety of materials that are present and their variations through the four profiles. The results for each deposit can be compared with the data given in the Report by Pollard and Barron.

Montgomery Deposit

The Report (p. 82) states that the bauxite is moderately hard and ranges in color from light grey to flesh pink. The top of the ore is generally clearly marked but grades upwards into a hard bauxite clay or into one consisting of a grey matrix of practically pure gibbsite containing reddish-colored material and white segregations of almost pure boehmite. The contact between the ore and the underlying clay, a pure, well-crystallized kaolinite, is generally distinct, but with veins of almost pure gibbsite penetrating the clay for several feet. These mineralogical statements are based on the previous X-ray analyses by one of us (G. W. B.).

The boehmite segregations noted above have been reexamined and their identification as boehmite confirmed. Such segregations are not found in the ore body itself, and boehmite is almost absent. It is possible to pick out hard white, grey-white, creamy-white and whitish materials at various levels, but they have no common mineralogical factor. From 0–4 feet, the hard white material is pure or nearly pure kaolinite, but from 4–6 feet the soft white component is 90 percent gibbsite, from 6–8 feet it is 30 percent kaolinite, 70 percent gibbsite, from 8–10 feet the grey-white material is 95 percent kaolinite, but between 10 and 12 feet a similar material is practically pure gibbsite. Creamy-white and similar material from 12–18 feet contains about 75 percent kaolinite, 25 percent gibbsite. Thus, white or nearly white material, which may be hard or soft, ranges in mineral content from nearly pure gibbsite to nearly pure kaolinite with various intermediate compositions. Moreover the changes seem to take place quite erratically. Even after many X-ray analyses of these materials had been taken, it was still impossible to forecast from the color and hardness of a material its true mineralogical character.

In this deposit the pink, buff, and pinkish-brown materials were predominantly gibbsite, and they contained about 1 percent of goethite which is probably the cause of the color. Anatase is found at every level to the extent of 1–2 percent. Boehmite is largely absent.

Nieu Haarden Deposit

The Report (p. 86) gives only one short paragraph on this deposit, which is now nearly worked out.

Here the most nearly white material is principally gibbsite, while the colored material is often, but not always, rich in kaolinite. Thus 0–2 feet is mainly pinkish and contains 60 percent kaolinite, from 8–10 feet, 10–12 feet, and 14–16 feet the material is pinkish-white and contains respectively 15, 10 and 40 percent kaolinite. The color probably comes from hematite and goethite. Between 12 and 14 feet, there is soft, brown, crumbly material containing 20 percent goethite, 25 percent hematite, 45 percent kaolinite.

Maria Elizabeth Deposit

The Report (p. 86–87) gives practically no data on the mineralogy of this deposit. It is described as mainly hard and grey. Figure 3 shows that kaolinite is largely absent apart from the uppermost and lowest levels. Anatase and boehmite are more noticeable at all levels than in the two previous deposits. Boehmite ranges from 1–2 up to about 10 percent between 8 and 10 feet, and anatase is present to the extent of about 1–4 percent. Pink color seems to be associated mainly with 1–2 percent goethite.

At several levels, it was possible to pick out segregations of pure white, soft material amounting to no more than a few percent of the whole sample. These were principally kaolinite. They occurred, for example, at 2–4 feet, 14–16 feet, 16–18 feet, 18–20 feet. On the other hand, whitish segregations at 8–10 feet were 75 percent gibbsite, 20 percent boehmite, and at 20–22 feet they were 55 percent kaolinite, 45 percent gibbsite. Again it was difficult to be certain from visual inspection whether a white segregation would be kaolinite or gibbsite, though generally the purest white material was kaolinite.

Warababaru Deposit

This deposit lies about 30 miles south of the area in which the previous three deposits are located. The Report (p. 91) describes this deposit as resembling those at Montgomery and states "it may be assumed that the origin of these deposits is similar to those at Montgomery." No mineralogical data are given.

Figure 4 summarizes the present results. Kaolinite is largely absent except in the upper layers, 0–8 feet, and in the lowest layer, 28–30 feet. The crystallinity of the kaolinite shows a marked variation between the 0–6 foot layers, and the 6–8 foot layer. In the former the kaolinite is of the lattice-disordered variety; it is hard and slightly "off-white" in color and is about 20 percent of the samples supplied. From 6–8 feet, the kaolinite is white and has a "soapy" feel and is very well crystallized. Parts of the X-ray diffractometer traces for these two kinds of kaolinite are shown in Figure 5; the striking difference between them is obvious. Electron micrographs were taken of these kaolinites but they showed surprisingly little difference. In both cases it was possible to pick out crystals of about 0.5 micron

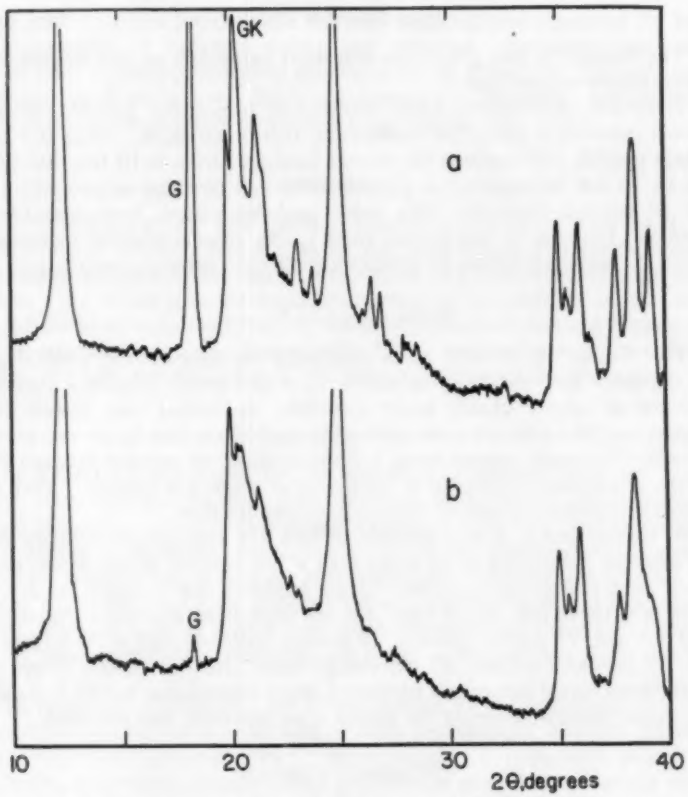


FIG. 5. X-ray diffractometer traces: (a) Well-crystallized kaolinite, plus gibbsite, 6–8 feet Warababaru deposit. (b) Disordered kaolinite, plus a trace of gibbsite, 0–6 feet Warababaru deposit. G = gibbsite reflection; GK = combined gibbsite-kaolinite reflection. Observe the well-resolved reflections in the range $2\theta = 20° - 27°$ in (a), and their replacement in (b) by a band of continuous scattering. Similarly in the region of $2\theta = 38°$, (a) shows much better resolution than (b).

size showing good hexagonal outlines. The explanation for these differences must be sought in the field evidence. Probably much more could be learned about the formation of the bauxite deposits from information of this kind, which reveals striking mineralogical differences not detectable in other ways. The rather plastic, white and yellowish, basement clay is a well-crystallized kaolinite with small proportions of gibbsite and goethite.

As in the other deposits, anatase is generally present to the extent of 1–2 percent, and goethite and hematite are present in varying proportions, ranging up to 10 percent in some of the darker brown materials. A few white segrega-

tions could be picked out that were hard in some layers and quite soft in others, and which in all cases were principally gibbsite. Between 8 and 10 feet a trace of mica was found, the only occasion on which mica was detected in these materials.

DISCUSSION

The results show the usefulness of applying a semi-quantitative X-ray analysis to these materials. The principal minerals are established and their approximate proportions. Gibbsite and kaolinite are the major components and anatase, boehmite, goethite, and hematite are the more common minor components. Quartz and mica occur very rarely and only in small proportions. The pink-brown color of these materials arises principally from goethite and/or hematite and these are generally associated with gibbsite rather than kaolinite. White material may be gibbsite, kaolinite, or a mixture of the two. White segregations, varying from pure white to various grey and creamy shades of white, and varying from a soft and soapy feel to a hard and brittle texture, may be either kaolinite or gibbsite, and it is impossible to tell from color and texture which mineral is present. However, segregations that are pure white and soft are nearly always a very pure, well-crystallized kaolinite. In fact, well-crystallized kaolinite seems to predominate in these deposits, although occurrences of disordered kaolinite are also found.

DEPT. OF CERAMIC TECHNOLOGY,
PENNSYLVANIA STATE UNIVERSITY,
UNIVERSITY PARK, PENN.,
Jan. 4, 1956

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MINERALOGY OF THE GIANT YELLOWKNIFE GOLD MINE, YELLOWKNIFE, N.W.T.[1]

LESLIE C. COLEMAN

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ABSTRACT

A suite of metallic minerals that occur in the extensive shear zone systems of Giant Yellowknife Gold Mines' property has been studied. The members of this suite appear to have been formed during three separate periods of mineralization from hydrothermal solutions having a magmatic origin. The introduction of these solutions is believed to have been effected by dilation of the shear zones that accompanied deformation of the surrounding rocks. The metallic minerals were probably formed from these solutions by a combination of reaction with, or replacement of, preexisting minerals, and precipitation in spaces opened by dilation.

Each of the mineralization periods is believed to have been characterized by a group of minerals and an environment of deposition different from those of the other two periods. Minerals formed during the first period are pyrite and arsenopyrite. Sphalerite, chalcopyrite and minor pyrrhotite were formed during the second period of mineralization and sulphides and sulphosalts containing Pb and Sb were the dominant minerals formed during the third and last period. The P-T conditions during mineralization are believed to have varied progressively from intense during the first period (temperatures exceeding 500° C accompanied by high pressures) to relatively mild during the third and last period (temperatures below 350° C and fairly low pressures). Since most of the gold is believed to have been introduced and deposited during the first mineralization period, the ore deposit is classed as hypothermal.

The most common and hence most important association of gold in the ores is with arsenopyrite. This association is believed to be a product of

[1] Part of a dissertation presented to the faculty of Princeton University in candidacy for the degree of Doctor of Philosophy.

time and space rather than the result of any type of chemical affinity. Other less common associations are with pyrite, gangue minerals, and the younger sulfides and sulfosalts. The mineral aurostibite is believed to be a reaction product formed by the interaction of S-deficient antimonial solutions with pre-existing gold.

There is a strong possibility that some of the gold was originally deposited in solid solution in pyrite and arsenopyrite. However, it seems unlikely that much of it now exists in such a state although there may still be appreciable ultrafine, dispersed gold intermixed with these sulfides.

INTRODUCTION

THIS work represents the results of a study of the ore mineralogy of the Giant Yellowknife property, which was carried out by the author during the period 1952–1955 for the management of Giant Yellowknife Gold Mines Limited.

During the study, particular attention was paid to the occurrences of gold in the ores and to its relationships with the other metallic minerals. Attempts were also made to pursue lines of investigation that would offer some evidence about the physical-chemical conditions that prevailed during mineral deposition, and as to the possible manner of ore emplacement.

It is hoped that the facts and hypotheses brought forth will prove of help in understanding not only the geology and treatment of the Giant ores, but also of similar ores from other properties in the area.

The Yellowknife mining camp is located on the west shore of Yellowknife Bay on the north arm of Great Slave Lake, with the town of Yellowknife at its center. The twenty-five claims that constitute the property of Giant Yellowknife Gold Mines Limited, the principal producer in the area and the fifth largest straight gold producer in Canada, are situated four miles north of the town of Yellowknife on the West shore of the bay.

Considerable work has been done on the geology of the area surrounding Yellowknife, and for comprehensive treatments of the geology of this region the reader is referred to works by Jolliffe (24), Henderson and Brown (22, 23), and Campbell (8, 9). For greater detail concerning the geology of the Giant property, the reader is referred to work by Dadson, Brown and Bateman (2, 5, 12).

PREVIOUS INVESTIGATIONS OF THE MINERALOGY OF THE YELLOWKNIFE AREA

The mineralogy of the ores of the Giant Yellowknife mine and of the Yellowknife camp in general has, in the past, been examined in varying detail by Ridland (35), Graham and Kaiman (16, 17), and the present writer (11). The suite of minerals identified by Ridland, on the basis of standard etch reactions and microchemical tests as outlined by Short (37), were somewhat revised by this author, the principal change being the elimination of the tellurides and sulfarsenides. Graham and Kaiman were the first to report the presence of aurostibite, a rare antimonide of gold, which is one of the most interesting minerals in the Yellowknife suite. Their other observations and proposed paragenetic sequence, agree in general with those already reported.

The conclusions reached in all these earlier investigations pointed to a close

association between the gold and the sulfantimonides. Ridland stated that "Of the metallic minerals, gold is most commonly associated with tennantite," and the present writer concluded that "Gold exhibits a close affinity with relatively low temperature minerals rich in antimony. The quantity of microscopically visible gold present in any one locality, appears to be greatest where such minerals are abundant." Paragenetically, gold was relegated by Graham, Kaiman, and the author principally to a late stage in the mineralization sequence, although it was pointed out that some of it probably formed contemporaneously with some of the earlier minerals. Ridland, on the other hand, stated that "A long period of deposition for gold is indicated by the variety of relationships it has with its associates . . . and (it) is believed to have deposited simultaneously with these minerals (pyrite, sphalerite and quartz)." Later, he mentions that "On the whole . . . gold and the sulphosalts show contemporary relationships."

There seems to be general agreement in these earlier works regarding the overall sequence of deposition of the other ore minerals. In each case it corresponds essentially to the normal sequence of mineral deposition as outlined by Newhouse (32), with pyrite and arsenopyrite earliest, followed by sphalerite and chalcopyrite, and with galena, stibnite and the sulfosalts forming in the late stages.

The views as to the continuity of deposition propounded by the different authors do, however, differ considerably. Ridland (35) seems to envision a single introduction of metal-bearing solution from which all the ore minerals were formed. He does, however, mention two parts of the "hydrothermal stage" separated by a period of fracturing. The tentative paragenetic sequence outlined by Graham and Kaiman (16) consists of two main periods of mineral formation, separated by a period of fracturing. They do not state whether they think that each stage represents a separate introduction of mineralizing solution. The present writer (11) postulated three distinctly separate stages of mineralization, each representing the introduction of a solution having a composition different from those that preceded it. He also stated that "minerals formed during each period incorporated elements from the earlier formed minerals (that they replaced)." The only mention of the manner of emplacement of these ore-forming solutions was made in the paper by this author (11). Dilation accompanying deformation was regarded to be an important factor in the emplacement of the ores, and the ores were considered to have formed essentially by the filling of dilatant zones which was accompanied by some replacement. The other authors also mention evidence of formation of ore minerals both in "open space" and by replacement.

The principal reference to the P-T conditions existing at the time of ore formations was made by Ridland who stated that the minerals present "suggest intermediate temperature deposition. Textures and structures suggest low-pressure deposition" (35). The present writer stated that "High formational temperatures seem improbable, although a depositional environment having temperatures in the order of several hundred Centigrade degrees is quite plausible" (11). No mention was made of the pressure conditions.

In all of the above studies, specimens that were examined had been col-

lected at random. In most cases the specimens were above normal in their content of metallic minerals, especially the sulfosalts, and were, therefore, by no means representative. The author, now, holds somewhat different views regarding the history of mineral deposition from those outlined above.

PROCEDURE FOLLOWED IN THE PRESENT INVESTIGATION

Specimens were collected from all readily accessible exposures of ore in the underground workings and surface outcrops of the Giant property. Wherever possible the places where they were obtained were located at intervals of 25 feet on the mine grid system. This interval was chosen in order to conform with the sections that are drawn up by the mine's geological office. Specimens were also collected in the vicinity of ore and in mineralized rocks containing gold that are not of ore grade. In each locality an attempt was made to collect a specimen that was representative of that region, and in addition any specimens that might be unusually rich in their content of metallic minerals. The place from which each specimen came was recorded using three co-ordinates—north-south, east-west, and vertical.

Each of these specimens was subsequently divided into two similar portions, one of which was sent to the assay office where it was analyzed for Au, S, As and Sb. The suite of specimens collected from one level of one orebody were also analyzed for Ag.

Polished sections were then made from about half the specimens, that is specimens from localities on sections spaced fifty feet apart. In regions where the mineralogy appeared to be of particular interest, polished sections were also made of the intervening specimens. Also sections were made from all specimens which contained unusually high amounts of Au, S, As or Sb, as indicated by the analyses. The final polish in all cases was obtained by using diamond abrasives of 8, 2 and ½ micron grades. These abrasives give an extremely fine polish with an absolute minimum of relief, even between minerals of such differing hardness as stibnite and pyrite.

A preliminary survey was then made of all the polished sections in which all minerals that could not be visually identified were identified by X-ray powder methods. Numerous checks by X-ray methods were also made on the visual identifications and in no case were they found to be in error. Subsequently, each section was reexamined in detail. By using stains that were selective for the minerals already identified in the particular section, any other minerals present were isolated and subsequently identified. At the same time, the textural relationships and the associations of the different minerals were noted.

For purposes of identification X-ray powder methods were employed exclusively because of their precise nature and because of the small amount of material that is required to make an identification. A number of minerals found in the Yellowknife ores have very similar assemblages of chemical constituents and, furthermore, react very similarly with chemical reagents. For this reason alone, X-ray methods are the only adequate means of identifying them. It was found that individual grains with diameters less than 5 microns

($\pm 6 \times 10^{-6}$ milligram by weight), could be identified by these means, so that even had their constituents and reactions to reagents been distinctive, these methods would have been by far the most satisfactory for purposes of identification.

In the identifications, a Phillips' powder camera, 57.3 mm in diameter, was employed using copper radiation and a nickel filter. Because of the minute size of the sample being identified, it was found that such a camera, with small diameter and a strong type of radiation as emitted by copper, was the most

TABLE 1

MINERALS IDENTIFIED AND THEIR RELATIVE ABANDANCE

Native Elements		
Gold	Au	+
Antimony	Sb	−− (Central and South ASD Zones)
		−−− (1) (Elsewhere)
Lead	Pb	−−− (12)
Sulfides		
Pyrite	FeS_2	++++
Marcasite	FeS_2	−−− (5)
Pyrrhotite	$Fe_{1-x}S$	+
Arsenopyrite	FeAsS	++++
Geradorffite	(Ni, Co, Fe)AsS	−−− (1)
Gudmundite	FeSbS	−−− (2)
Ullmannite	NiSbS	−−− (7)
Sphalerite	ZnS	+++
Chalcopyrite	$CuFeS_2$	+++
Galena	PbS	−
Stibnite	Sb_2S_3	− (Central and South ASD Zones)
		−−− (2) (Elsewhere)
Antimonide		
Aurostibite	$AuSb_2$	−
Sulfosalts		
Boulangerite	$Pb_5Sb_4S_{11}$	−−
Meneghinite	$Pb_{13}Sb_7S_{28}$	−−− (1)
Jamesonite	$Pb_4FeSb_6S_{14}$	++
Berthierite	$FeSb_2S_4$	++ (Central and South ASD Zones)
		−−− (1) (Elsewhere)
Chalcostibite	$CuSbS_2$	−− (Central and South ASD Zones)
		−−− (1) (Elsewhere)
Bournonite	$PbCuSbS_3$	++
Tetrahedrite	$(Cu, Fe, Zn, Ag)_{12}(Sb, As)_4S_{13}$	++

satisfactory. If a larger camera or weaker radiation had been used, the required exposure times would have been excessive. As it was, an average exposure was in the order of 12 hours.

In collecting specimens for identification, a glass fibre approximately 0.05 mm in diameter, is mounted on a brass spindle that can be set in the axle of the camera. The glass fibre is dipped in grease of medium viscosity (stopcock grease was found quite satisfactory), and touched to any clean object so that excess grease will flow off leaving a thin film on the fibre. The mineral

to be identified is scratched with a very sharp needle under the microscope. The powder generated by the scratch is picked up on the end of the mounted fibre. The specimen then can be identified.

The selective stains used for visually differentiating various minerals and for enhancing textural relations, were obtained from data listed in works by Short (37) and Uytenbogaardt (40). Head and Loofbourow (21) describe a selective stain for bournonite that was also extensively used, and which, it was found, stained other copper-bearing minerals to a much lesser degree.

GENERAL MINERALOGY

Minerals Identified.—During the present study 192 specimens were examined in detail. These had been collected from the B-Shaft (Northwest, North Central and Northeast Ore Zones) and C-Shaft (South and Central ASD Zones) areas. An additional 51 specimens, which had been collected from the A-Shaft area and the West, Brock and A Zones, were examined in less detail.

In all, 22 metallic minerals which are believed to be of hypogene origin were identified. They are listed in Table 1 with an indication of their relative abundance, using the following notation:

++++	Ubiquitious and in large proportions.
+++	Almost ubiquitous but seldom present in large proportions.
++	Common, sometimes present in large proportions.
+	Common but generally not a major constituent.
−	Common but usually present in only minor amounts.
−−	Fairly common, usually present in only minor amounts.
−−−	Only present in a few specimens (the number of occurrences is noted after them in parentheses) and generally only in minor amounts.

Spatial Variations of Mineralogy.—Mineralogical investigations indicate a general lack of zoning of the metallic minerals that occur in the shear zones underlying the Giant property. These investigations suggest the following conclusions concerning the distribution of mineral species in the Giant ores:

1. The distribution of individual mineral species is random.
2. Only a few species occur in any one specimen—seldom more than six or eight.
3. In a single locality the mineral species present tend to be the smallest number that would be required to use up all the chemical constituents that are present.

Therefore, it appears that the different mineral associations that were formed in the Giant ores were more a function of local composition than of temperature or pressure.

The only suggestion of zoning noted is in the Sb and Pb content of some of the later minerals. Figures 1–4, depict that zoning which does appear to

exist. Three groups of minerals are plotted on these diagrams:

	Symbol	Mineral Group
a)	□	Minerals rich in Sb and containing no Pb (native antimony, stibnite, berthierite, chalcostibite)
b)	×	Minerals containing Sb, in which Pb is either absent or is not a preponderant cation (jamesonite, bournonite, tetrahedrite)
c)	●	Minerals in which Pb is a major cation and in which Sb is either absent or a relatively minor constituent (native lead, galena, meneghinite, boulangerite)

Specimens that were examined in detail and in which none of the above minerals occur are denoted by an open circle.

As can be seen in the diagrams, the evidence for zoning is more suggestive than apparent, with that in Figure 1 being the most pronounced. Groups (a) and (c) appear to be mutually exclusive. The former is almost totally restricted to the South and Central ASD Zones with its only other observed occurrences being in specimens from the 409 Lower Orebody (Fig. 2). At the time the writer collected his suite, these latter specimens represented the northernmost underground exposures of ore. It is possible, therefore, that one or more zones in which these minerals are important constituents have been opened up by more recent mining.

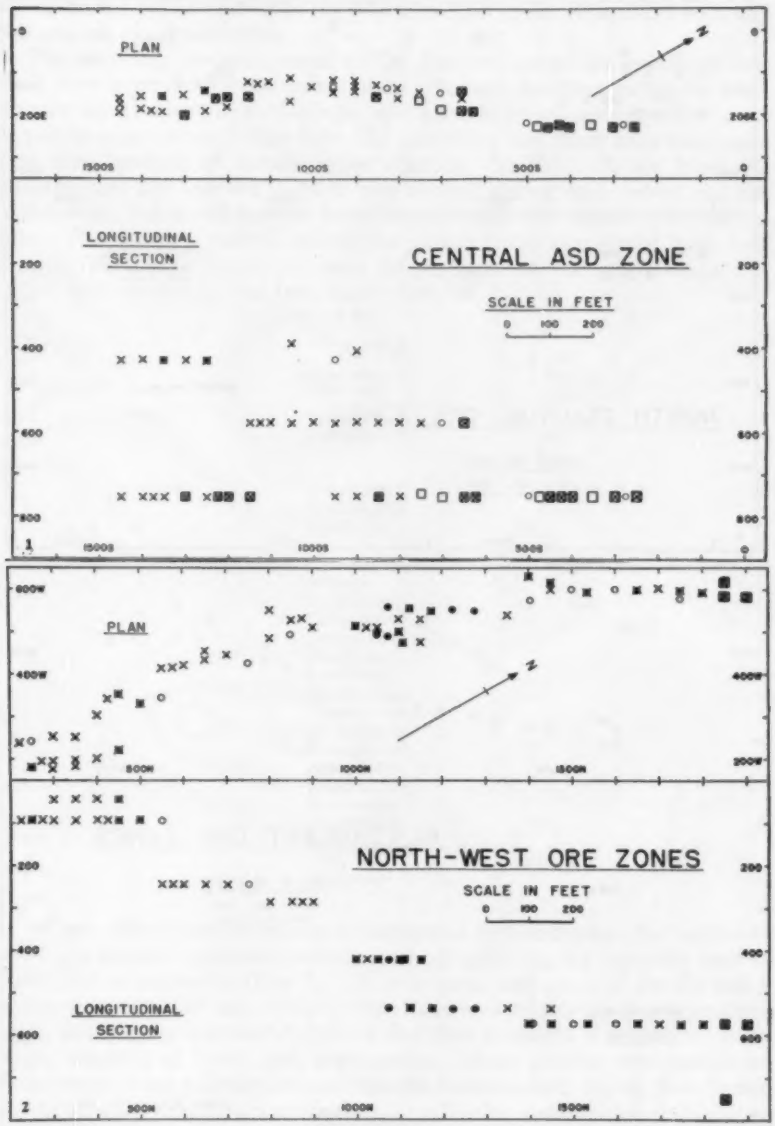
Minerals of group (c) are almost totally absent in specimens from the South and Central ASD Zones (Fig. 1), but are fairly common in other parts of the mine.

If the suggestions of mineral zoning indicated by these diagrams are a reality, they probably have little, if any, economic significance, because, as will be dealt with in a later section, the minerals containing Pb and Sb are believed to have been formed later than most of the gold. Furthermore, as far as the presence or absence of ore (gold) is concerned, the spatial distribution of any other mineral, or minerals, appears to have little or no meaning.

Paragenesis.—The position of gold and of aurostibite in the paragenetic sequence will be discussed in the section entitled "Gold Associations and Their Implications." This is done because of the complexity of the position of these minerals and also because of their economic importance.

The present investigations suggest that there have been at least two major periods of metallic mineralization within the ore zones. The basis for this concept is primarily textural. The degree to which much of the pyrite and arsenopyrite has been deformed, fractured, and granulated, as compared to the other metallic minerals suggests their formation at a considerably earlier date. Much of the sphalerite and chalcopyrite was probably deposited before the formation of the minerals containing Pb and Sb. Thus, it would seem that there have been either three periods of metallic mineralization, or two periods with the second divided into two substages.

At this point it might be well to define the author's concept of "period of mineralization." A period of mineralization is considered to be a time interval during which introduction of constituents and/or their deposition was taking place continuously. Furthermore, it is believed that a considerable time in-


PLAN
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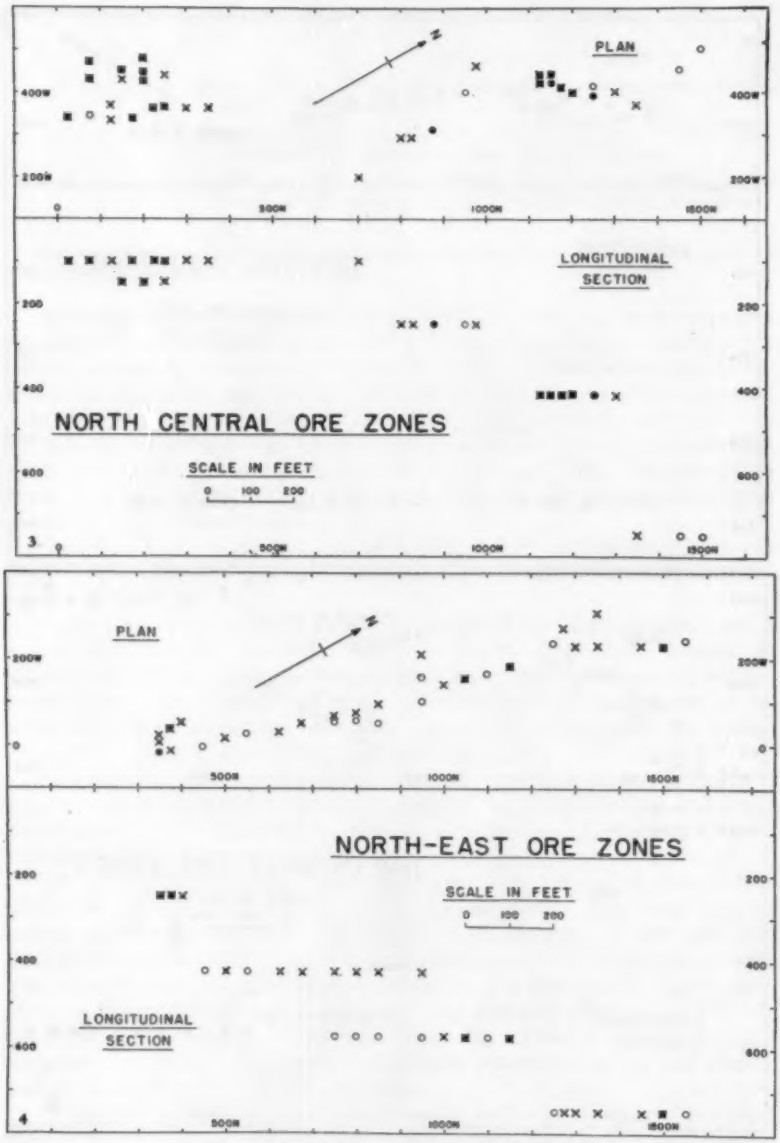
2

FIGS. 1 and 2.



FIGS. 3 and 4. Longitudinal section and plan views which give a suggestion of zoning based upon the indicated positions of the three different mineral groups.

terval, during which neither of the processes took place, elapsed between any two periods of mineralization.

For simplicity, the paragenesis will be discussed adopting the concept that there were three periods of mineralization. It must, however, be kept in mind that the last two may be only substages of a single period and may have overlapped to some extent. Also there is a possibility that there have been more than three periods of metallic mineralization. In Table II are listed the minerals that are believed to have been formed during each period and the constituents that would have to have been introduced to permit their formation. This assumes that all constituents, apart from these, could have been derived from pre-existing minerals by replacement and resorption. The author believes that this has been largely the case.

TABLE 2

Period	Minerals Formed	Constituents Introduced
First	Pyrite	Fe
	Arsenopyrite	As
		S
Second	Sphalerite	Zn (Cd, Mn)
	Chalcopyrite	Cu
	Pyrrhotite	
Third	Galena	Pb
	Stibnite	Sb
	Gersdorffite	Ni (Co)
	Ullmannite	
	Gudmundite	
	Marcasite	
	Sphalerite	
	Pyrrhotite	
	Chalcopyrite	
	Boulangerite	
	Meneghinite	
	Jamesonite	
	Chalcostibite	
	Bournonite	
	Tetrahedrite	
	Berthierite	
	Lead	
	Antimony	

Where stibnite and berthierite are associated with each other, the berthierite generally contains scattered inclusions of older Fe-bearing minerals such as pyrite and arsenopyrite (Fig. 5). It is believed that much of the Fe and S within the berthierite was obtained from these earlier minerals during replacement, and that the scattered inclusions represent remnants of what were much larger amounts of pyrite and arsenopyrite. More positive evidence of incorporation of pre-existing material into the later minerals during their formation is offered by numerous occurrences of sulfosalts in association with chalcopyrite. In most instances where Cu-free sulfosalts, such as jamesonite and berthierite, are associated with chalcopyrite, sulfosalts containing Cu, such as tetrahedrite, bournonite and chalcostibite, occur between the two minerals.

The appearance of these latter minerals in such instances suggests that they have been formed as reaction rims between chalcopyrite and the younger Cu-free sulfosalts.

It would seem unlikely that the process of fractionation, indicated above, would be complete, and hence it is probable that each mineralizing fluid con-

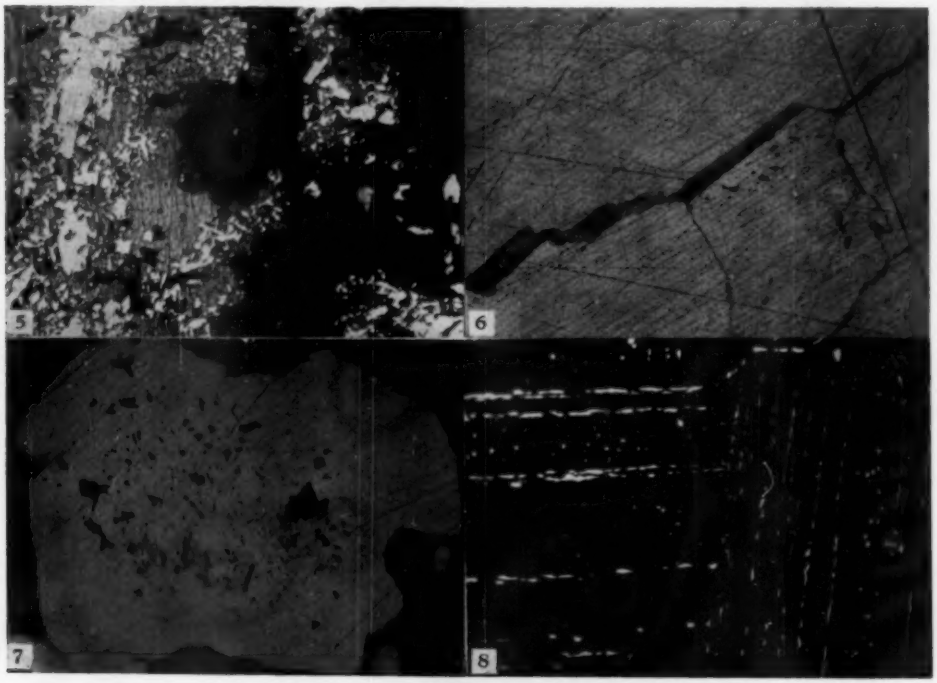


FIG. 5. Partially digested arsenopyrite (white) in berthierite (gray), × 240. 750 level, 625S, 190E.

FIG. 6. Jamesonite (dark gray) filling a fracture in pyrite (light gray); some replacement of pyrite by jamesonite at the right, × 240. 575 level, 650S, 145E.

FIG. 7. Tetrahedrite (dark gray) corroding pyrite (light gray), × 115. 425 level, 1100S, 120E.

FIG. 8. Oriented inclusions of chalcopyrite (white) in sphalerite (gray) presumed to be a product of exsolution, × 225. 100 level, 250N, 180W.

tained minor concentrations of elements that were present in earlier fluids in much higher concentrations.

As was previously mentioned, the postulation of a considerably older age for much of the pyrite and arsenopyrite with respect to the other metallic minerals is based largely on deformational textures. In addition, numerous instances were noted in which these two minerals are veined by or have been corroded by the other metallic minerals (Figs. 6, 7). Also, irregularly

scattered remnants of pyrite and arsenopyrite within the younger sulfides and sulfosalts are by no means uncommon. In every case, all the textural evidence for the time relationship of arsenopyrite and pyrite to the other metallic minerals suggests that these two minerals are older.

The later metallic minerals have been subdivided into two groups and are believed to have formed either during two distinct periods or during two substages of the same period. This idea is supported by considerable evidence which, however, is not as satisfactory as that which delineates these minerals from pyrite and arsenopyrite. Much of the evidence suggests reaction and resorption by which minerals containing Pb and Sb have formed from the reaction of fluids containing these constituents with pre-existing sphalerite, chalcopyrite, and a minor amount of pyrrhotite, as well as with pyrite and arsenopyrite.

Sphalerite and chalcopyrite in polished section, unfortunately, do not reveal evidence of subjection to deformation after deposition. Unlike pyrite and arsenopyrite, they do not possess a crystal form that is readily apparent and thus the results of deformation, fracturing or granulation, could not be easily discerned. Therefore, deformational textures prove unsatisfactory for differentiating the age of these two minerals from that of the sulfosalts and younger sulfides. Although the anisotropism of pyrrhotite should indicate whether or not that mineral has been subject to deformation, the size of pyrrhotite particles associated with the sphalerite and chalcopyrite of the second period was so small that this type of evidence could not be used.

A number of cases were noted in which sphalerite and chalcopyrite were veined by sulfosalts and younger sulfides. The major evidence for disparity of age was what appeared to be reaction rims of the sulfosalts and youngers sulfides about sphalerite and chalcopyrite, and what were apparently remnants of them within sulfosalts and younger sulfides. Not all relationships of these two minerals conformed to the above sequence and some evidence was noted that suggested some of the sphalerite and chalcopyrite, and much of the pyrrhotite, had been formed during the third period of mineralization. Therefore, the writer believes that the formation of these three minerals took place during both the second and third mineralization periods.

Sphalerite, especially, appeared to have been formed at more than one time and there appears to be, furthermore, more than one type of sphalerite in the ores. The first, and presumably older, type displays a dark reddish internal reflection under crossed nicols and commonly contains oriented inclusions of chalcopyrite (Fig. 8). Some sphalerite under crossed nicols exhibits a honey-colored internal reflection. This variety does not contain any chalcopyrite and, on the basis of textural evidence, appears to have been formed late in the mineralization history of the ores. These observations agree with similar observations made on other ores by other investigators (10, 25, 30, 36). Their work, and especially that of Neumann (30) and Kullerud (25), suggests that the two types of sphalerite have different FeS contents and hence were formed under different conditions—the darker colored sphalerite, which is richer in FeS, being formed at higher temperatures and thus earlier than the honey-colored sphalerite. This agrees with the writer's concepts.

The metallic minerals that are believed to have been formed during the third period of mineralization, exhibit little, if any, evidence of having been subjected to deformation after their deposition. Well-developed crystals, especially of the acicular sulphosalts, are not uncommon. Wavy extinction under crossed nicols was observed occasionally on some of the anisotropic minerals, but it is believed that very little post-depositional deformation would be required to produce this phenomenon. Hypidiomorphic equigranular textures are not uncommon and are believed to indicate an unstressed post-depositional history. A few of these late minerals, such as gudmundite, may exhibit granular textures that could be interpreted as the result of deformation. In view of the weight of other evidence, a more likely explanation is that this is a relic texture inherited from a pre-existing mineral. In the instance cited, it is believed that gudmundite formed by the reaction of Sb-bearing fluids with pre-existing, granulated arsenopyrite.

The minerals believed to have been formed within any single period of mineralization, exhibit, for the most part, conflicting mutual relationships, or else relationships that suggest contemporaneity (Fig. 8). The anomalies are reasonable in view of the assumption made in the previous section—the local mineralogy is more a function of composition than of temperature or pressure. During a single period of mineralization, any one locality might receive several fresh accessions of mineralizing fluids. Although each of these "pulses" might originally have had similar compositions, their compositions on reaching a particular locality would be expectably different since they would have passed through different environments. If they had not actually traversed different channelways, they would have traversed regions in which material had been either deposited or removed by the preceding "pulses."

The only minerals that appear to have a uniformity of relationship to other minerals formed during the same mineralization period are the native elements —lead and antimony—and aurostibite. Aurostibite will be considered later. The occurrences of lead and antimony invariably suggest that they have formed from trapped residues of mineralizing fluids. That is, they have been formed only after all the S in their immediate vicinity had been used up in the formation of their neighboring minerals. Thus, in any one locality, they would be the last metallic minerals to form, and would only be preserved to the present if no fresh access of S-bearing fluid reached that locality.

GOLD ASSOCIATIONS AND THEIR IMPLICATIONS

A marked revision of prevailing concepts regarding the relative importance of the different gold associations, and also the paragenetic position of gold, in Yellowknife ores is regarded as necessary on the basis of the results of this investigation. It is believed that the current ideas concerning some, if not many, other gold ores might also merit consideration.

In the author's previous work on Yellowknife ores (11), it is stated that the principal gold association is with the sulfosalts. Because of this it was believed that most of the gold was formed late in the paragenetic sequence and penecontemporaneously with the sulfosalts. Ridland (35) stated that "A long

period of deposition for gold is indicated by the variety of relationships it has with its associates." However, the general impression that he conveyed was that most of the gold had been formed relatively late and at the same time as the sulfosalts.

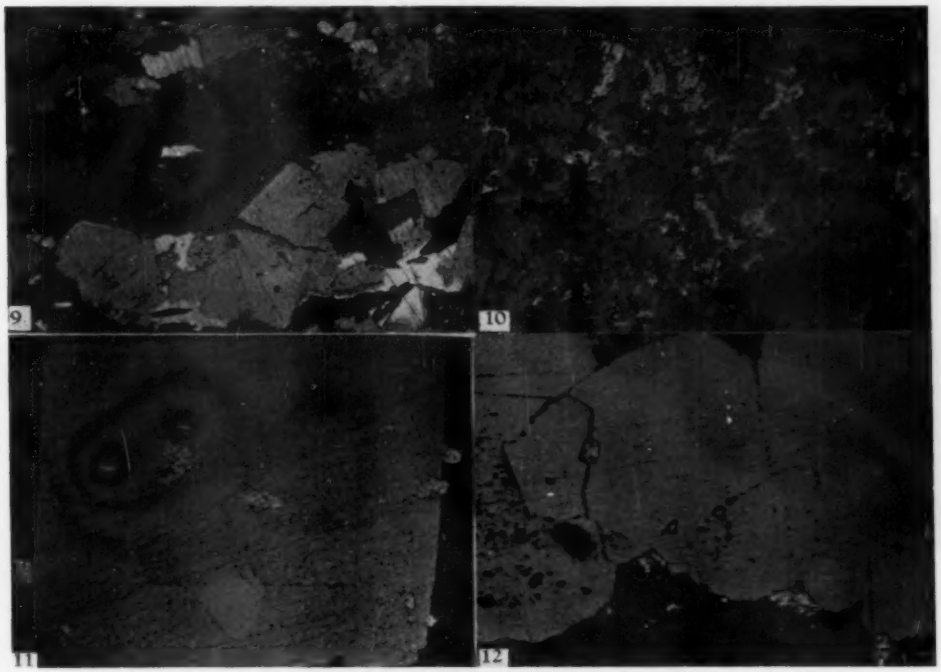


FIG. 9. Gold (white) filling fractures in, coating and replacing arsenopyrite (gray), × 300. 250 level, 800N, 295W.

FIG. 10. Gold (white) in arsenopyrite (gray), × 300. 560 level, 1125N, 555W.

FIG. 11. Particles of gold (pitted white) in pyrite (gray), × 320. 425 level, 1025N, 490W.

FIG. 12. Gold (white) in pyrite (light gray) and bournonite (dark gray); the bournonite appears to be corroding and replacing the pyrite and the gold within it looks as though it may originally have been included in the pyrite, and have been remobilized during the pyrite replacement; most of the gold particles in the pyrite are rounded and exhibit no relationship to any fracture, × 420. 100 level, 300N, 190W.

The writer's present views are that some of the gold may have been introduced during each period of mineralization but that most of the gold was introduced and deposited before the third and last period.

The most common association of gold in the Giant ores is with arsenopyrite (Figs. 9, 10). The gold generally either fills fractures in, or forms thin

coatings on, arsenopyrite crystals. In a few specimens, it appears that it may have replaced some arsenopyrite. Although the majority of the gold in the ores is associated with arsenopyrite, the major part of the arsenopyrite does not appear to have gold associated with it. In many specimens in which gold is associated with arsenopyrite, the association is spotty and no gold is observed with much of the arsenopyrite in the specimen. In such specimens, the arsenopyrite with which the gold is associated is generally that which is finest grained—i.e., either that which commenced crystallization relatively late, or that which has been most extensively granulated and fractured.

A common, but quantitatively much less important, gold association is with pyrite in which it commonly fills fractures. Another common and very interesting mode of occurrence is as discrete rounded blebs in pyrite that appear

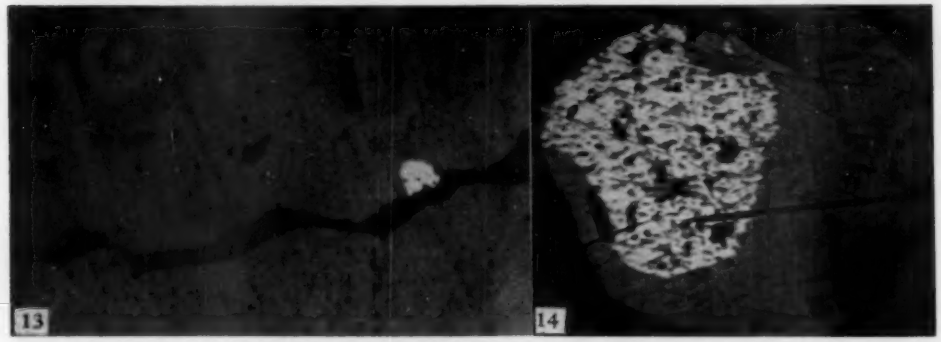


FIG. 13. Sphalerite (dark gray) filling fracture in pyrite (light gray); the fracture follows the border of an included arsenopyrite crystal (lighter gray) at lower left, and the border of a gold particle (white) at right; the arsenopyrite was present before fracturing as was probably the gold; the fracture may have been localized by these included minerals whose presence could have produced a line of weakness in the pyrite. × 600. 425 level, 1050N, 500W.

FIG. 14. Aurostibite (light gray) which contains some tetrahedrite (dark gray) armouring gold (pitted white), × 1000. 560 level, 1125N, 555W.

to have no relation to any fracture or channelway (Figs. 11, 12). The latter suggests that some of the gold may have crystallized contemporaneously with the pyrite, either in solid solution or as trapped residues around which the pyrite crystals grew.

Gold commonly occurs as discrete particles in the gangue, especially quartz, which have no apparent association with any other metallic minerals. The quartz surrounding these particles often exhibits evidence of strain or fracturing under polarized light.

The last typical occurrence of gold is with the younger sulfides and sulfosalts. In these associations, the gold occurs commonly in rounded or subrounded bodies that may be totally enclosed by a single grain of the associated mineral, or, which transect intergranular boundaries. The appearance of the

gold in these associations suggests either a relic character or contemporaneous deposition. In the latter case, much of the gold may have been remobilized by the fluids from which the associated minerals formed. No occurrence was observed in which gold appeared to be definitely younger than any of these associated minerals.

Observed associations of gold and aurostibite (Figs. 13, 14 and 16) suggest that aurostibite is younger than the gold, and has formed by reaction of antimonial solutions with gold that was already in the solid state. Typical occurrences of aurostibite are as coatings or rims on gold particles, or as what appear to be reaction rims between gold and apparently younger sulfides or sulfosalts. In no case was gold observed with a core of aurostibite.

There is some evidence that other constituents of the mineralizing fluids, besides Sb, may have reacted with pre-existing gold. A number of occurrences of gold of a distinctly reddish color were observed. In all instances there were associated Cu-bearing minerals. This reddish gold commonly occurs as coatings on particles of gold having a normal hue. It seems reasonable to suggest that it is a Au-Cu alloy which has formed as the result of reaction of fluids containing Cu with pre-existing gold. Similar "red gold" has been reported in other areas (14) and its color has been shown to be the result of a content of Cu. Investigations have indicated that complete mutual solubility between gold and copper (42) exists at or above about 290° C.

The associations of gold in the Giant ores, as outlined above, conflict with the concept of "Late Gold" (29) which has enjoyed some popularity in the past. A perusal of the literature concerning gold ores, also uncovers numerous references (10, 13, 15, 18, 20, 33, 36, 39, 41) to gold which is intimately associated with sulfides and which is believed to have been introduced largely at the same time as these sulfides. As Haycock (20) points out "there appears to be a well-marked tendency for very finely divided and sub-microscopic gold to occur when the deposition was contemporaneous with that of the host, and, conversely, a tendency for coarser gold to occur when its deposition was later than that of the host." The writer believes that some of this latter coarser gold, in the case of the Giant ores at least, may have originally been the finer type which was deposited contemporaneously with the older sulfides and was reworked and redeposited by later mineralizing fluids so that it now appears to be very much younger than its original host.

Schwartz (36) has considered in some detail the nature of the relationship between gold and its associated minerals. He cites a number of cases in which these associated minerals are believed to have acted as precipitants in causing the deposition of gold. His summation, with which the author agrees, is:

> As a result of a comprehensive review of the literature as well as personal studies, the writer is impressed with the small amount of replacement of the minerals with which gold is associated. Gold does occasionally replace the host minerals but certainly this is the exception rather than the rule. . . . It is difficult to see how a mineral could act as an effective precipitant unless it entered into the reaction. If it did react then the minerals being precipitated including gold, should replace the host minerals, unless the precipitation is indirect. Grout has shown that gold will be precipitated from an acid solution when mingled with an alkaline

solution which has dissolved many of the most common sulfides. This may explain the scales of gold which often occur on sulfides which have not necessarily been affected. Warren suggests the possibility of an electro-chemical effect which should not be ruled out, but the actuality of the process seems very difficult to determine. Taking into account the variety of host minerals for gold and the irregularity of the relation in gold ores, the writer is inclined to the conclusion that most host minerals do not act as effective precipitants but are hosts because of fortunate association in time and place plus a limited precipitating effect, such as is suggested in the above review.

Figure 15. - Effect of CdS and MnS Solid Solution on Cell Length of Sphalerite

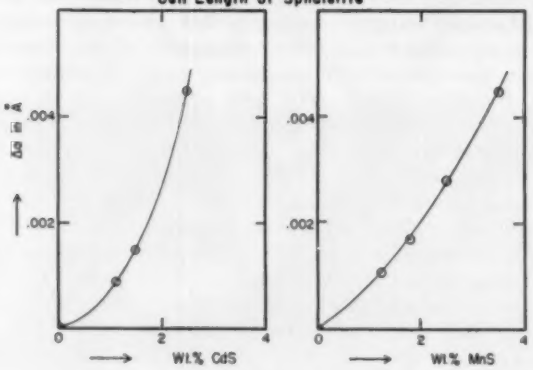
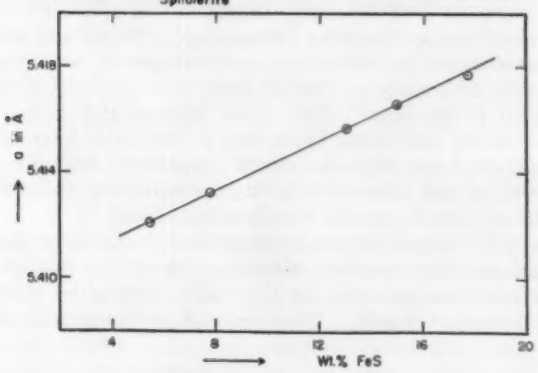


Figure 16 - Cell Length vs Composition of Fe-Bearing Sphalerite



The possibility of gold occurring in solid solution in sulfides had been proposed by several investigators in the past (7, 26, 27, 39). Kuranti (26) claims to have made pyrite artificially with up to about 64 ounces per ton of gold in solid solution. Unfortunately his information is only available in abstract. Maslenitsky (27), who supplies more detailed information, synthesized pyrite and pyrrhotite containing as much as 10 ounces per ton of in-

visible (submicroscopic) gold. The suggestion is that while the gold may not be in actual solid solution in these sulfides, it occurs in such a highly dispersed manner that it closely approaches that state. Maslenitsky states, "Chemical investigations have shown that only negligible amounts of gold are recovered from the pyrite with the aid of mercury and cyanide solutions, notwithstanding a very fine reduction of the pyrite, the use of oxidants and a prolonged contact with the solvents." This has rather important metallurgical implications. He found that preliminary heating of polished sections as described by Burg (7), coalesced the gold into aggregates which could be seen easily under the microscope and which resembled the appearance of gold encountered in the pyrite of certain deposits. His descriptions of these gold segregations suggest that they are very similar to the small rounded blebs of gold encountered in some of the pyrite in the Giant ores.

As Stilwell and Edwards (39) point out, "Since . . . pyrite (is a) non-stoichiometric compound, it seems likely that any gold solid-solution that occurs in (it) will be of the limited interstitial type of solid solution, found in some metals, in which the solute atoms fill vacant spaces in the lattice structure, rather than substitute for solvent atoms" (in this case, iron). This view was supported by Kuranti's work (26) in which it was shown that the lattice constant of pyrite changed continuously with increasing gold content up to a limiting amount—2,000 grams (about 64 ounces) of gold per ton of pyrite. Peacock and Smith (34) demonstrated that pyrite could have a sufficient number of vacant ion sites (sulfur in the formula could be as low as 1.98) to allow solid solution of this much gold. It is possible that in various pyrites having varying departures from the stoichiometric ideal, the limitation of the gold solid-solubility would vary. If solid solution of gold in pyrite did take place in the Giant ores, it appears that it remained well within the permissible limits.

Because of the important metallurgical implications that would accompany a solid solution of gold in sulfides, several lines of experimental investigation were pursued on a number of ore specimens from the Giant property. Specimens chosen for these investigations were ones that assayed between 1.0 and 3.5 ounces of gold per ton, and in which no gold had been microscopically visible.

Three lines of approach were adopted in the investigation of these specimens that might contain "invisible" gold:

1. Polished sections were heated for several hours at 600° C and then re-examined. Both Maslenitsky (27) and Burg (7) had heated their specimens in evacuated tubes to prevent oxidation and to permit escape of any sulfur vapor that might be emitted by the specimen. If the sulfur vapor remained in contact with the specimen, it was found that gold sulfide might be formed. The method used by the author was different but it was believed that the same conditions were obtained. The specimens were heated in an inert atmosphere—nitrogen—which was flowing steadily over the specimen during the heating process so that any sulfur emitted would be removed from contact with the specimen. The principal behind this method of aggregation of dispersed gold in sulfides is believed to be that of auto-annealing in which energy is supplied to a frozen-in unstable material to permit its rearrangement into an energetically more stable state.

2. Metallic concentrates were obtained from the specimens by heavy liquid separations and these concentrates were treated with strong acids to dissolve any sulfides. The residues were then examined microscopically. The specimens were first boiled in concentrated nitric acid. Half of the residue from this process was subsequently boiled in concentrated hydrochloric acid. The remaining half from the first process and the residue of the second process were each subjected to a heavy liquid (acetylene tetrabromide) separation. The heavies, middles, and lights from each of these separations were examined separately.

3. An attempt was made to examine polished surfaces of specimens under an electron microscope using replica techniques. Dry-stripping methods were employed using solutions of formvar in chloroform and in dioxane. These proved unsatisfactory. It might be possible to obtain satisfactory replicas of such surfaces by using collodion and by floating off the resultant film by immersion in water. Such a technique would, however, allow no control of the exact portion of the surface to be examined. Because of these difficulties, the electron microscope approach was abandoned.

The results of the first line of experimental approach were rather inconclusive. In most of the specimens that were heated some gold was observed after treatment, which had not been visible previously. However, the amount of gold that was "made visible" appeared to be totally insufficient to account for the assays. Segregations of gold were noted only in a few of the pyrite grains, and in no case was there more than one segregation observed in any one grain. This would suggest that if any gold is in solid solution or a highly dispersed state in the sulfides, it is so only in some of the pyrite and is not so in any of the other sulfides.

Considerable gold was observed in the residues from the processes employed in the second line of approach. The gold particles were typically ovoid in shape. This suggested that any grinding of the specimen before its treatment in acid had not affected the nature or size of the gold particles since otherwise one would expect them to be considerably flattened. The diameters of the gold particles observed ranged from 2–50 microns but the majority had diameters less than five microns and many more were 5–10 microns in diameter. Gold particles were observed in all fractions examined. The heavy fractions contained by far the most gold particles and those that had been treated with both HNO_3 and HCl contained more than those that had just been treated with HNO_3. The size distribution of the gold particles in the specimens investigated suggests that some of the Giant ores do not conform to the size distribution curves developed by Haycock (20) for most Canadian gold ores, but instead have size distributions that are appreciably displaced towards the submicroscopic and colloidal ranges. However, it is not believed that the curves are displaced sufficiently to indicate that any appreciable amount of gold is now in solid solution in the sulphides.

The combined results of the experimental approaches that were pursued suggest that while there may now be some gold in solid solution in the sulfides of the Giant ores, it is probably only a very minor portion of the total gold present in these ores. The nature of much of the fine-grained gold that occurs

in the ores suggests that at one time much of it may have been in solid solution in the sulphides but was subsequently aggregated into microscopically visible particles by some process similar to auto-annealing.

P-T CONDITIONS DURING MINERALIZATION

The general nature of the Giant orebodies—their wide extent, their general lack of zoning, their persistence with increasing depth, and the character of their major mineral constituents—suggests that the P-T conditions that prevailed during most of the mineralization were intense and that these conditions became gradually milder with each successive period.

Previously, it was thought that ores of this area belonged to Lindgren's low mesothermal category. This idea was based largely on the lead sulphantimonide association. It is now believed that this suite of minerals represents the product of a late stage in the mineralization which occurred long after the essential formation of ore (emplacement and deposition of gold). Furthermore, it is believed that the presence of minerals of this suite is not necessarily indicative of low temperatures and pressures during mineralization.

The literature contains a number of references (1, 15, 28, 33) to gold ores containing minerals that are believed to indicate high temperatures of formation, which also contain sulphosalts and other so-called low temperature minerals—tellurides, stibnite, galena. It must be remembered that, as in the Giant ores, these latter minerals were probably formed late in the mineralization history of each of these ores and hence their environment of deposition was probably much less intense than that which accompanied the greater part of the mineralization. Bowen (3) states that the melting points of specific minerals place an upper limit on their temperature of formation. Furthermore, the melting point of any mineral will be lowered by the presence of other minerals that are soluble in the liquid phase of that mineral, or in the liquid phase produced by the incongruent melting of that mineral. Thus jamesonite, which melts incongruently at 609° C would, as Bowen points out, probably have formed even from a dry melt, at less than 500° C if other sulfides were present. Similarly with other sulfides and sulfosalts present in the Giant ores, for which melting point data (3, 19) are available, one arrives at maximum temperatures of formation of about 450° C. for stibnite (M.P. = 546–551° C) and chalcostibite (M.P. = 552° C) or higher for pyrite, pyrrhotite, arsenopyrite and sphalerite.

According to Smith (38), if pyrite is anisotropic in polished section it has formed at a temperature less than 135° C. He states:

> It was inferred that iron replacing sulphur in sulphur-deficient pyrite may be in regular positions, giving optically anisotropic pyrite, or it may be in irregular positions, giving the isotripic variety. The regular replacement may be made random by heating above 135° C and this change is irreversible over the short period of laboratory experiments. It is probably irreversible in nature since isotropic pyrite with a deficiency of sulphur does occur. The hypothesis is presented that pyrite formed in nature above approximately 135° C was isotropic and remained so when cooled to room temperature, but when formed below this temperature it was anisotropic.

If Smith's hypothesis is valid, practically all the minerals in the Giant ores would have formed at temperatures below 135° C since most, if not all, of the pyrite is markedly anisotropic. To test the hypothesis a number of Giant specimens were heated for periods up to six hours at temperatures of about 600° C. In no case was the anisotropism of the pyrite affected. Therefore, Smith's hypothesis appears to be invalid for Giant ores at least, and the anisotropism of pyrite, for the present at least, cannot be used uncritically as a geological thermometer.

In dealing with the problem of the temperature of formation of the Giant ores, one is not confined solely to speculation and hypothesis. Kullerud (25) has shown that the FeS content of sphalerite formed in the presence of an excess of FeS is a function of the temperature of formation, and that this content can be used as a geological thermometer. Since sphalerite in the suite of Giant specimens is present only in small amounts and is generally intimately intergrown with other metallic minerals, determination of FeS content by chemical analysis is unsatisfactory.

However, it had been found by Kullerud that the cell dimension of sphalerite is a function of FeS content. Unfortunately the X-ray data that he provided (25) are in error since the a-value used for his standard (NaCl) is incorrect. Dr. Kullerud very kindly supplied the author with several analyzed specimens of sphalerite with FeS contents ranging in weight percent from 5.5 to 17.7. The cell dimensions of these specimens were measured with a wide angle spectrometer using Cu radiation and silicon as an external standard. The a-value obtained for each specimen had to be corrected for CdS and MnS content, since these constituents have an appreciable effect on the cell dimensions of sphalerite. Data obtained from Kullerud (25) (Fig. 15) were used in making this correction. The corrected a-values were plotted against weight percent FeS (Fig. 16). Using data obtained from Table XIV of Kullerud's paper (25) the weight percent FeS in sphalerite was plotted against the temperature of formation (Fig. 17). This had been determined synthetically by obtaining unmixing temperatures of sphalerites with varying FeS contents. The data on Figures 16 and 17 were combined (Fig. 18) to give a graph of cell dimensions of sphalerite (corrected for CdS and MnS content) versus temperature of formation. It must be kept in mind that, if anything, a temperature of formation obtained from Figure 18 will be a minimum. With the exception of the content of CdS and MnS, for which corrections have been made, all factors (lack of equilibrium, exsolution of chalcopyrite, etc.) would operate to give a temperature lower than that which had existed at the time of formation.

The cell dimensions of sphalerites from seven specimens collected from widely scattered places in the Giant orebodies were measured. A semiquantitative spectrographic analysis was made for the Cd and Mn contents of the specimens. The measured a-values were corrected using the maximum possible amounts of CdS (0.10 wt.%) and MnS (0.02 wt.%) that the sphalerites could contain, as indicated by the analysis. The corrected a-values indicate temperatures of formation ranging between 365° C and 560° C for these sphalerite specimens.

The specimens of Giant sphalerite on which the above measurements were made are all of the variety that is believed to have been formed during the second period of mineralization. Most of the sphalerite formed during this period contains exsolution blebs and lamellae of chalcopyrite (Fig. 8). Experimental work by Buerger (6) indicated that the temperature of unmixing of chalcopyrite from sphalerite in some specimens he studied had been 350–

Figure 17 - Solvus Curve of Fe-Bearing Sphalerite

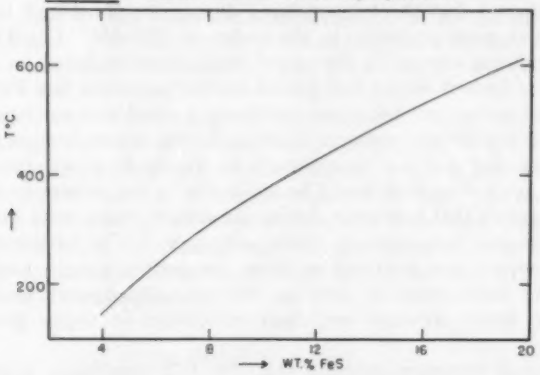
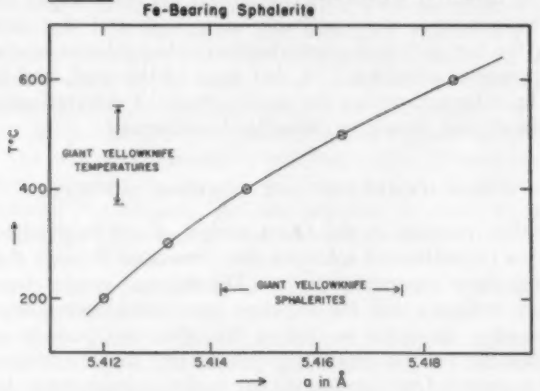


Figure 18 - Cell Length vs Temperature of Formation of Fe-Bearing Sphalerite



400° C. Although this unmixing temperature would be a variable dependent on the composition of the system, it is believed that the Giant chalcopyrite-sphalerite unmixing temperature would not be much different from that which Buerger determined. Thus, two different lines of evidence indicate that the temperature during the second period of mineralization exceeded 360° C and probably during part of the period was greater than 500° C.

Since most of the gold in the Giant ores is believed to have been introduced and deposited prior to the deposition of the sphalerite of the second period, the above results would suggest that the ore (used in the true sense of the word) is hypothermal and hence that an appreciable spatial extent would be expectable. Furthermore, if high temperatures obtained during introduction and deposition of much of the gold, it would become more probable that some of the gold deposited in solid solution in the sulfides than if formational temperatures were considerably lower.

It is believed that the temperatures during the third and last period of mineralization were probably in the order of 250–350° C. This figure is purely speculative except for the upper limit, which is based on the fact that the sphalerite formed during this period appear to contain less FeS than those of the second period and hence were probably formed at lower temperatures.

The evidence for the pressure existing during mineralization is much less definite than that for the temperature in as much as no good geological barometers are known that would be applicable to the present case. Textural evidence suggests that pressures during the earlier stages were quite high and that they became progressively lower with time. The earlier minerals are typically compact and fractures in them are generally tight and thoroughly healed. The later minerals, such as the sulfosalts, appear to have formed under much lower pressures and their occurrence in vuggy growths is not uncommon.

The overall evidence suggests that the P-T conditions existing during mineralization of the Giant orebodies underwent considerable progressive variation with time. It is believed that during the early stages pressures and, especially, temperatures were probably quite high and that both decreased until during the last period of mineralization only moderate temperatures and fairly low pressures prevailed. In that most of the gold, and hence ore, is believed to have formed during the earlier stages of mineralization, it is proposed that the deposit should be classed as hypothermal.

EMPLACEMENT OF THE METALLIC MINERALS

The metallic minerals in the Giant orebodies are believed to have been deposited from hydrothermal solutions that circulated through the shear zone system during three separate periods. The mineral species formed at each of these times indicates that the solutions introduced during any one period had a composition dissimilar to that of the other two periods. The author postulates that the process producing this variety of mineralizing fluids has been one of magmatic fractionation similar to the endomagmatic hydrothermal differentiation of Neumann (31).

The constituents from which the metallic minerals were formed are believed to have been derived from a magmatic source. This is not incompatible with the ideas of Boyle (4) although he postulates a different source for the quartz of the orebodies than that postulated by the author for the metallic constituents. It is proposed that the magmatic emanations that introduced

these metallic constituents were Boyle's "migrating solutions . . . (from which were) . . . precipitated the silica as quartz veins and lenses" (4). Although Boyle shows that this silica was probably derived from the wall rocks, it is not believed that the metallic constituents, with the possible exception of some of the Fe, came from the same source since they exhibit no distribution similar to that of the silica. The writer believes that the solutions that effected the local migration of silica were the transporting media for the metallic constituents and were derived from the same magmatic source as these constituents.

Boyle's work (4) has provided some evidence as to the nature of the mineralizing fluids. The evidence he presents suggests that they were mildly acidic aqueous solutions containing CO_2 and S (4, Fig. 7) and possibly some alkali metals.

The emplacement of these solutions is believed to have been effected by dilation of the ore zones that resulted from deformation of the surrounding rocks. The lowering of the hydrostatic pressure, which such dilation would cause, would permit entry of solutions propelled by high pressures such as would exist in a magma. The metallic minerals were then deposited by a combination of reaction or replacement and precipitation in relatively open space. There is abundant textural evidence to support this hypothesis of a dual mechanism of mineralization.

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DEPT. OF GEOLOGY,
LAFAYETTE COLLEGE,
Jan. 29, 1957

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EZCURRITE ($2Na_2O.5B_2O_3.7H_2O$), A NEW SODIUM BORATE FROM ARGENTINA: OCCURRENCE, MINERALOGY, AND ASSOCIATED MINERALS[1]

SIEGFRIED MUESSIG AND ROBERT D. ALLEN

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ABSTRACT

Ezcurrite ($2Na_2O.5B_2O_3.7H_2O$) is a new sodium borate mineral discovered at the Tincalayu borax mine in the Province of Salta, Argentina. The mineral is associated with borax and kernite; ulexite and inderite also occur in the borate sediments. Tincalconite occurs as a weathering product of borax. Ezcurrite looks like kernite and has the following properties: Sp. Gr. = 2.153; ns (Na) $\alpha = 1.472$, $\beta = 1.506$, $\gamma = 1.526$; biaxial negative; 2V (calc) 73½°; Z $\wedge$ elongation 42.6°. It contains: B_2O_3, 58.21%; Na_2O, 20.73%; H_2O, 21.06%. The X-ray powder pattern shows the three most prominent d spacings to be 6.94A, 3.08A, and 2.77A. The results of the differential thermal analysis are given. The deposit in which ezcurrite occurs has been deformed and is predominantly massive recrystallized borax. The borax was probably recrystallized during the deformation and some of it dehydrated under elevated temperatures to form kernite. Ezcurrite, which is less hydrous, was probably also formed at about the same time by crystallizing from solutions released by the dehydration of borax or kernite perviously formed. The temperature necessary to form ezcurrite might or might not have been higher than that for forming kernite. If the temperature was high enough, metakernite might have been formed. Some evidence indicates that the inderite at the deposit is primary. The mineral is named for Sr. Juan Manuel de Ezcurra, manager of the Cia. Productora de Boratos, S.A., owner of the Tincalayu mine.

[1] Published with the permission of Cia. Productora de Boratos, S.A.

Introduction

EZCURRITE is a new sodium borate mineral from the Tincalayu borax mine in the province of Salta, Argentina. It is associated with borax ($Na_2O.2B_2O_3.10H_2O$) and kernite ($Na_2O.2B_2O_3.4H_2O$), both of which were reported from Tincalayu by Ahlfeld and Angelelli in 1948 (1). Before 1948, kernite had been reported only from the Kramer district, California (13). Inderite ($2MgO.3B_2O_3.15H_2O$) also occurs at Tincalayu; elsewhere it is known to occur only in the Kramer district (7) and in Russia (2).[2] Ulexite ($Na_2O.2CaO.5B_2O_3.16H_2O$) and secondary tincalconite ($Na_2O.2B_2O_3.5H_2O$) are also found at Tincalayu.

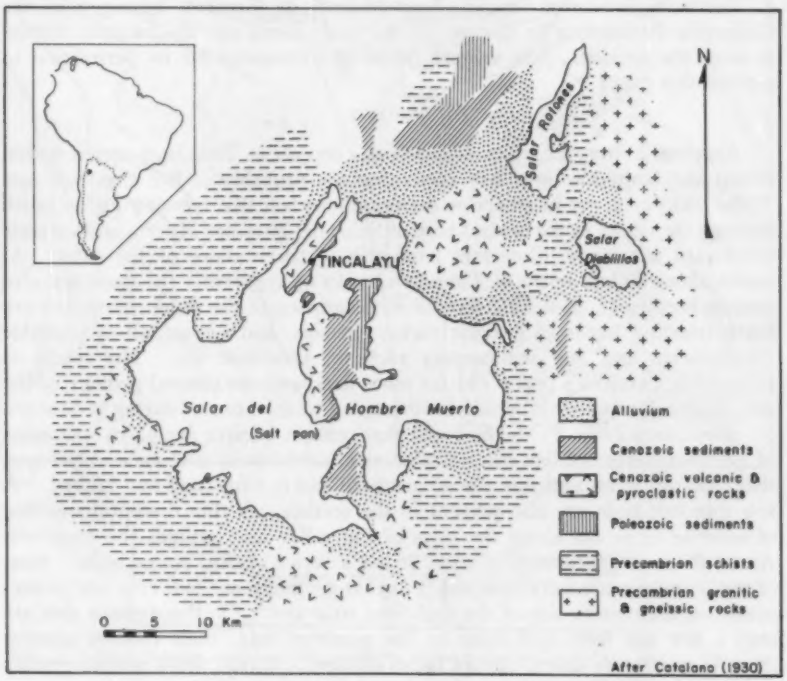

FIG. 1. Geologic index map of the Tincalayu borax deposit.

Tincalayu is on a peninsula that projects southward into the northern part of Salar del Hombre Muerto (Fig. 1). The mine is at an altitude of about 4,000 meters and is 146 km by road south of Pocitos station on the trans-andean General Belgrano railway.

Ezcurrite was originally discovered in 1941 by Messrs. L. D. Osborne and

[2] The inderite reported by Heinrich (9) from the U. S. is from an unknown locality and probably came from another country.

H. P. Gower during exploration work at Tincalayu. All specimens were lost, however, and the only record that remained was a chemical analysis in the files of the Compañia Productora de Boratos, S.A. In 1955 Muessig visited the mine in private interest in the hope that the new mineral could be found again. Unfortunately, the mineral could not be collected in place, but specimens of it were found on the mine dumps.

Although the authors share the responsibility for the contents of this paper, Allen is primarily responsible for the X-ray, DTA, and optical data, and Muessig for the remainder.

Ezcurrite is named for Sr. Juan Manuel de Ezcurra, Manager of the Compañia Productora de Boratos, S.A., which owns and has recently started to mine the deposit. The writers thank that company for its permission to publish this paper.

GEOLOGY

Regional Setting (*Fig. 1*).—The borax deposit at Tincalayu occurs within folded and faulted sedimentary rocks that are probably of late Cenozoic age. These rocks crop out in a narrow discontinuous belt that trends roughly north through the island in the central part of Salar del Hombre Muerto and extends northward for many kilometers from the northern shore of the salar. At places about 50 km. north of Tincalayu, rocks of apparently the same age also contain borates (1, 3, 4, 5). To the west and east of the sedimentary belt are north-trending bands of granitic rocks, gneisses, and schists, all of probable Precambrian age, and sedimentary rocks of Paleozoic age. The reader is referred to Catalano's paper (5) for more details of the general geology of the area under discussion, especially with regard to the borate-bearing sediments.

Mine Area (*Fig. 2*).—The rocks that contain borates are playa sediments of predominantly reddish-colored siltstones, sandstones, and some claystones, that crop out in an anticline whose northern end is bifurcated and faulted. A few thin tuff beds are also present in the section. A thin discontinuous bed of inderite crops out along the sides of the valley and outlines the structure. About 20 m stratigraphically below it lies a series of thin borax beds. Most of the sediments are salty, and red beds that contain much salt crop out prominently on the eastern side of the anticlinal structure. On the western side are only a few salt beds, and none on the northern side; their relative absence there is apparently due to abrupt facies changes. Basalt flows unconformably overlie the sediments to the north and west.

Borax Deposit (*Fig. 3*).—The deposit is a pluglike tabular massive body of predominantly clear and crystalline borax; measured along a northeast line, it is less than 10 m thick and has only a few thin red siltstone and sandstone layers in it. Underground, little stratification can be seen in the crystalline body, but at the margins the borax content diminishes abruptly and the intercalated and enclosing red sediments dip steeply away from the body in several places. At the end of one of the western drifts on the first level of the mine the edge of the ore body is a fault contact. Borax veins cut the otherwise barren sediments at many places at the margins of the ore body.

The axial plane of the ore body dips very steeply to the northeast nearly

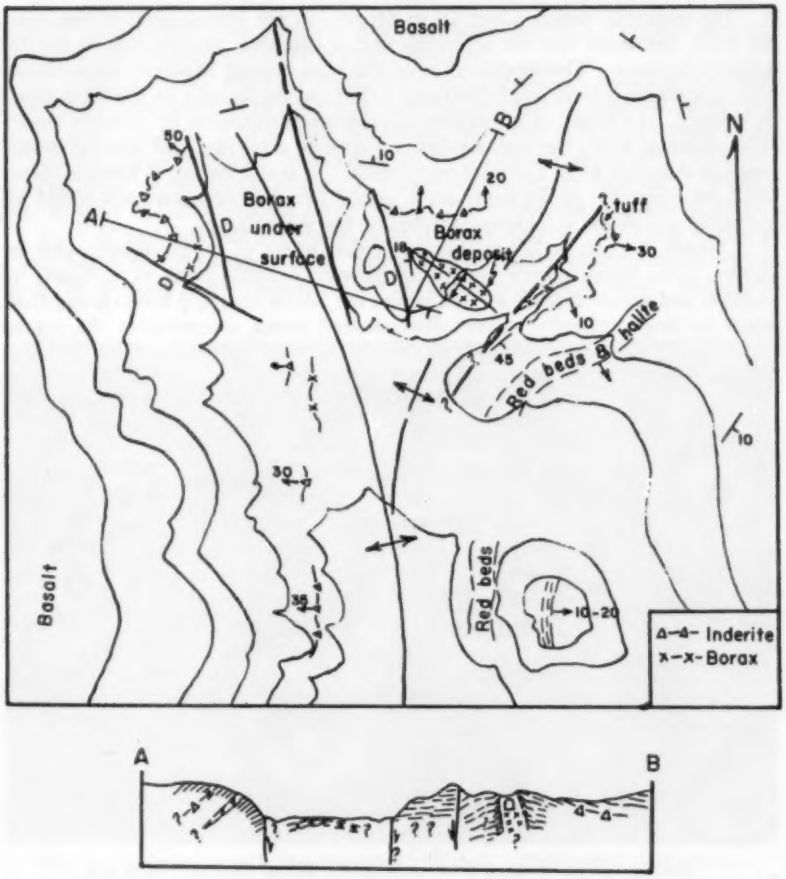

FIG. 2. Sketch map showing the geologic setting of the Tincalayu borax deposit.

at right angles to the eastern branch of the bifurcated anticline. From the attitudes of the sediment outcrops and the discordant relations of the ore body to the enclosing sediments, it seems likely that the ore body is in a faulted block that transects the structure. Moreover, the subsurface structure within the block appears to be tightly anticlinal and may be diapiric.

Mineral Occurrences.—Massive borax is the predominant mineral of the ore body and it has associated with it the new mineral, ezcurrite, and kernite. Kernite occurs as a few cluster up to about a meter across, completely surrounded by massive borax at a depth of about 20 m below the surface, on the second level of the mine.

The ezcurrite occurs about 10 m deeper, on the lowest level of the mine. In 1955, this level was not accessible and it was thus not possible to see the mineral in place. The specimens from the mine dumps, however, indicate that the ezcurrite occurs in much the same fashion as the kernite on the level above it, namely, as clusters of crystalline aggregates surrounded by massive borax. The physical and chemical similarity between ezcurrite and kernite would suggest that they have a similar occurrence. It is not known if kernite occurs with the ezcurrite on the lower level, as the two minerals were not found together in any of the specimens collected on the mine dumps.

Outside the ore body are thin lenticular layers of borax, ulexite and inderite. The borax occurs chiefly as discrete crystals lying in a matrix of reddish and greenish siltstone and shale; the borax in single beds ranges from small to large amounts. Some disseminated borax accompanies the crystal

FIG. 3. View looking northwest at the borax deposit. Men are standing at portal of first level adit.

beds and also occurs alone. The borax crystal layers may be the source bed for the massive borax of the ore body. Interestingly enough, however, the crystal layers are about 20 m stratigraphically below an inderite bed, whereas the top of the massive borax in the ore body is only about 5 m stratigraphically below the same inderite bed.

The inderite referred to above consists of intergrown crystals that are singly terminated and are up to 10 cm across, in a discontinuous bed less than a meter thick (Fig. 4). That the isolated outcrops lie at a single stratigraphic horizon is affirmed by their constant close association with distinctive green siltstones and shales, and tuff beds, and by their uniform stratigraphic distance from other beds that were traced in the field.

Irregular masses of puffy ulexite accompany the inderite in many places. Ulexite also occurs alone as white disseminations and thin irregular beds in the sediments, chiefly below the inderite horizon.

A white powdery crust of tincalconite has formed on borax where this mineral has been exposed to the atmosphere on outcrops, in mine workings, and on the mine dumps. Tincalconite also coats the pieces of kernite on the mine dumps, but this is probably contamination, as the kernite exposed in the mine is unaltered. Menzel and Schulz (12) have shown that on hydration, kernite goes directly to borax without going through the metastable tincalconite phase.

Most of the ezcurrite specimens have a white coating consisting of finely crystalline borax and tincalconite. These minerals are probably contamination from the dumps, which consist chiefly of borax and tincalconite. However,

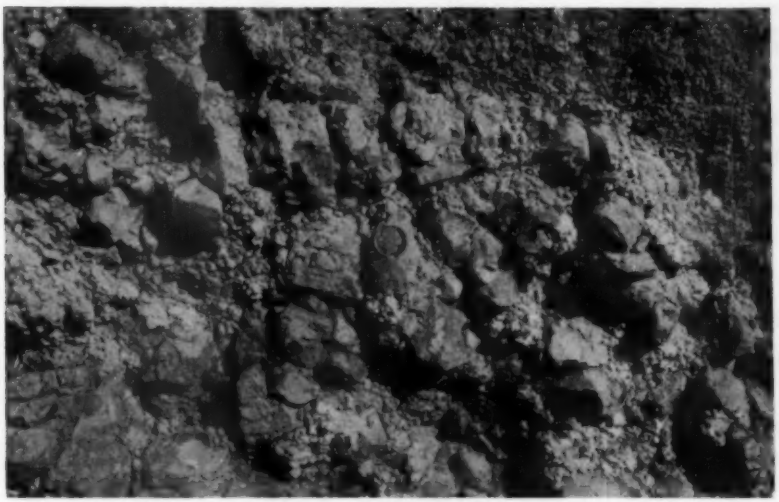

FIG. 4. Inderite crystals in green clay and shale. White spots are ulexite.

some of the finely crystalline material also occurs along minute cracks and cleavages within the coarsely crystalline ezcurrite and it is likely that it resulted from contaminating solutions while exposed on the dumps. A thin section gives no evidence that ezcurrite hydrated to the finely crystalline borax and tincalconite along cleavage cracks.

MINERALOGY

Ezcurrite occurs as intergrown easily cleavable masses that are moderately striated and have a bladed fibrous structure, some of which is radiating. Individual masses are up to 7 cm long and 1.5 cm wide. Two cleavages, one

perfect, and the other less so, intersect at an angle of 71° 18.5′ (average of 14 goniometer measurements ranging from 71° 06′ to 71° 31′). These cleavages form bent columnar fragments. A poorly developed cleavage meets the zone axis of the other two at a large oblique angle. The cleavages of ezcurrite are much like those of kernite, even as to angle, the two perfect cleavages of kernite, {100} and {001}, meeting at an angle of 71° 08′.

Ezcurrite is colorless and transparent and has a vitreous to satiny luster; it looks much like kernite. In hand specimen, ezcurrite can be differentiated

TABLE 1

OPTICAL PROPERTIES OF EZCURRITE AND KERNITE

	Ezcurrite	Kernite (Schaller, 13)
αNa	1.472 ± 0.002	1.454
βNa	1.506 ± 0.002	1.472
γNa	1.526 ± 0.002	1.488
Birefringence (γ-α)	0.054 ± 0.004	0.034
	Biaxial negative (−)	Biaxial negative (−)
2V	73½° (Calc.)	80°
Habit micro.	Prismatic cleavage fragments, untwinned	Cleavage fibers
Orientation	$\gamma\Lambda$ elongation: 42.6°, the average of ten measurements ranging from 42.2° to 42.9° $\beta\Lambda$ elongation: 47.4° (by difference)	$\alpha\Lambda c$: 38½° $\beta\Lambda c$: 51½°
Elongation	Positive	Positive
Other	Fragments with maximum extinction angle between γ and elongation, i.e., 42.6°, show acute bisectrix figures and permit measurement of both β and γ. Fragments with parallel extinction do not show centered interference figures and permit measurement of α' and γ'. α was measured statistically. The apparent lack of coincidence between optical directions and probable crystallographic axes suggests that ezcurrite is triclinic.	Cleavage fibers show parallel extinction. $r > v$, distinct.

from kernite by its slightly more satiny luster and its more noticeably bent cleavages. Hardness is about 2.5; specific gravity, as measured by suspending clear fragments in a mixture of bromoform and toluene, is 2.153. On heating over a gas flame it clowly swells to an opaque white cauliflowerlike mass, which on further heating fuses to a clear glass. Ezcurrite is very slowly soluble in cold water, slowly soluble in hot water, and easily soluble in acids.

Optical Properties.—The optical properties of ezcurrite and kernite are summarized in Table 1.

TABLE 2

X-RAY DATA FOR EZCURRITE AND KERNITE: INTERPLANAR SPACINGS AND RELATIVE INTENSITIES

Cu/Ni; λ = 1.5418A; patterns prepared with diffractometer from 2θ = 5° to 90°

Ezcurrite				Kernite			
d (A)	I	d (A)	I	d (A)	I	d (A)	I
8.98	1	2.24	<1	7.76	<1	2.26	<1
7.69	<1	2.21	<1	7.41	10	2.25	<1
6.94	10	2.14	<1	6.63	8	2.23	<1
5.50	<1	2.10	<1	6.01	1	2.21	1
5.28	<1	2.09	<1	4.67	<1	2.19	<1
4.82	<1	2.04	<1	4.30	<1	2.09	<1
4.48	2	2.02	<1	4.23	<1	2.08	<1
4.20	<1	1.994	<1	3.90	1	2.05	<1
4.04	<1	1.955	<1	3.80	<1	2.00	<1
3.80	<1	1.903	<1	3.70	3	1.957	<1
3.31	2	1.890	<1	3.51	<1	1.914	1
3.22	<1	1.802	<1	3.44	<1	1.884	<1
3.19	<1	1.793	<1	3.36	<1	1.821	<1
3.13	2	1.734	<1	3.31	<1	1.781	<1
3.08	6	1.692	<1	3.25	2	1.746	<1
2.99	<1	1.670	<1	3.13	1	1.722	<1
2.86	<1	1.642	<1	2.88	2	1.685	<1
2.77	3	1.590	<1	2.78	<1	1.626	<1
2.68	<1	1.540	<1	2.68	<1	1.435	<1
2.64	<1	1.480	<1	2.61	1	1.419	<1
2.59	<1	1.459	<1	2.57	<1	1.375	<1
2.53	<1	1.416	<1	2.51	<1		
2.45	<1	1.374	<1	2.47	4		
2.36	1	1.215	<1	2.39	<1		
2.32	<1	1.112	<1	2.34	<1		
2.29	<1			2.31	<1		

X-ray Data.—X-ray powder patterns of ezcurrite and kernite were prepared with nickel-filtered copper radiation over the range $2\theta = 5°$ to 90°, the spectrum being scanned with a diffractometer at 1° per minute with a time constant of 4 seconds. These X-ray patterns are presented in Table 2.

TABLE 3

CHEMICAL ANALYSES OF EZCURRITE AND KERNITE

(In percent)

	1	2	3	4
B_2O_3	58.86	59.34	58.21	51.02
Na_2O	20.67	20.37	20.73	22.66
H_2O	(20.47)	20.89	21.06	26.32
	100.00	100.60	100.00	100.00

1. Ezcurrite, water by difference. Ralph Mathieson, analyst. Qualitative tests for NH_3, P_2O_5, SO_4, Cl, F, and CO_2 were negative: Hy Almond, analyst.
2. Ezcurrite. Henry Kramer, analyst.
3. $2Na_2O \cdot 5B_2O_3 \cdot 7H_2O$, theoretical ezcurrite.
4. $Na_2O \cdot 2B_2O_3 \cdot 4H_2O$, theoretical kernite.

CHEMICAL ANALYSES

Chemically, ezcurrite is much like kernite, but it has slightly less water of crystallization and its constituents have different combining ratios. Chemical analyses of these two minerals are presented in Table 3.

According to the analysis (Table 3, no. 1) of ezcurrite, the molecular ratios are: Na_2O—0.3334; B_2O_3—0.8452; H_2O—1.1360; or: Na_2O—1.000; B_2O_3—2.536; H_2O—3.408.

A spectrographic analysis made by Hal W. Johnson, Pacific Spectrochemical Laboratory, Los Angeles, California, is tabulated below, in percent.

XO.O	B, Na
X.O	not reported
O.X	not reported
O.OX	Si, Al
O.OOX	Ag, Fe, Ca, Cu
O.OOOX	Mg

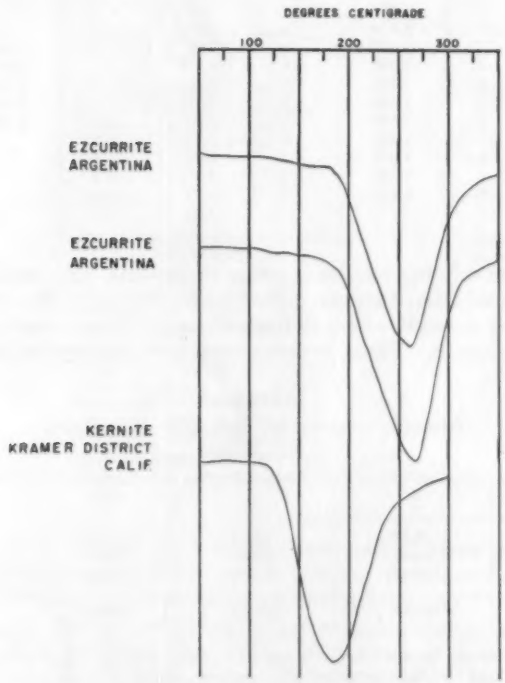

FIG. 5. Differential thermal analyses curves of ezcurrite and kernite. Heating rate: 30° C per minute; medium sensitivity.

DIFFERENTIAL THERMAL ANALYSES

Two differential thermal analysis curves of ezcurrite were prepared from data obtained using a portable differential thermal analysis unit, manufactured by the Eberbach Corporation. An earlier model of this portable unit was described by Hendricks, Goldich, and Nelson (10). The mineral was sieved to minus 50 plus 200 mesh and heated at a rate of 30° C per minute, starting with a cold furnace. This heating rate was maintained with the following voltage settings of a variable transformer: 50–200° C, 82 volts; 200–300° C, 85 volts; 300–350° C, 90 volts. The medium sensitivity adjustment gave satisfactory instrumental response. The ezcurrite curves, and for comparison, a curve of kernite from the Kramer district, California, are given in Figure 5.

The principal data supplied by these curves are summarized as follows:

	Initial temperature of endothermic reaction (°C)	Endothermic trough temperature (°C)
Ezcurrite	160 to 170	260 to 265
Kernite	100	185

DISCUSSION

Ezcurrite and the two accompanying borates, kernite and borax, as viewed in the light of their different waters of crystallization and their occurrence in different geologic environments, shed considerable light on the genesis of the Tincalayu borate deposit. This genesis, as outlined below, is consistent with both the field and laboratory data, and also with the genesis of the other known like deposit, that at Kramer, California.

Borax was deposited as crystals in a *salar*, or salt pan, together with red clastic sediments and some salt, a process that seems to be still going on today in several *salares* in Argentina. The borax in beds outside the ore body (Fig. 2), which are only slightly deformed and contain no kernite or ezcurrite, still occurs in the form of the primary crystals. The borax was buried under other sediments, which included borax and ulexite, and probably also inderite, which may be a primary mineral at this place.

After burial, the sediments were folded and faulted. At the ore body—in which kernite and ezcurrite occur—deformation was more intense than elsewhere and the original borax was probably pushed upward into a pluglike mass and was recrystallized from discrete crystals to a massive form. As the deposit has not been bottomed, the source bed of the massive borax is not certainly known.

Some of the borax dehydrated to form kernite, which is a higher temperature mineral (13, 12).. Ezcurrite, which is the least hydrous of the three sodium borates discussed here and retains its water of crystallization to higher temperatures than the other two borates, probably also formed at about the same time by crystallizing from solutions released by the dehydration of borax or of kernite previously formed. In solution, the stable transition point of borax to kernite is 58.2° C at atmospheric pressure (12).

The temperature necessary to form ezcurrite might have been higher or lower than that for forming kernite. But temperature was probably not the only variable factor that determined which of the sodium borates formed; the relative amounts of Na_2O, B_2O_3, and H_2O available at the place and time of new-mineral crystallization might finally have determined which of the minerals formed: recrystallized borax, kernite, or ezcurrite.

Experiments in the system Na_2O–B_2O_3–H_2O have not produced ezcurrite to date, and hence its temperature of formation at atmospheric pressure is not known. Until it is known, nothing can be said regarding the highest temperatures reached at the ore body during deformation. Further, when this is known, it might be possible to speculate whether the synthetic *metakernite* ($Na_2O.2B_2O_3.2H_2O$(11)) should have formed and should be looked for at Tincalayu.

The structural setting of the ore body indicates that higher pressures, and therefore higher temperatures at constant volume, probably existed only here during deformation. That recrystallized borax, and the less hydrous forms, kernite and ezcurrite, occur nowhere else in the area is consistent with the above inference.

In many respects, the Tincalayu deposit is like the sodium borate deposit at Kramer, California. At Kramer, kernite is associated with primary borax and both Schaller (13) and Gale (8) regard its presence as evidence of elevated temperatures. There also, the kernite is associated with much recrystallized massive borax, whereas in areas where kernite does not occur, the borax is predominantly in the form of euhedral crystal layers. Inderite is now also known at Kramer (7), but its occurrence is different from that at Tincalayu and may or may not have bearing on the genesis of the deposits as viewed from a standpoint of their mineralogical similarity. Ezcurrite has not been found at Kramer, but it might well occur, especially in the deeper parts of the deposit.

The Tincalayu deposit differs further from that at Kramer in being more deformed, and in not having the associated arsenic and antimony minerals, nor the calcium, and sodium-calcium borates, colemanite and probertite. Moreover, the salty sediments, such as occur at Tincalayu, are strikingly absent at Kramer. (Did NaCl play a role in the formation of ezcurrite at Tincalayu?)

There is no conclusive evidence that the inderite at Tincalayu is primary, and it has not been found forming under surface conditions anywhere in the world. Some lines of evidence, however, suggest that the inderite is primary: 1. It occurs chiefly as aggregates of well-formed singly terminated crystals at one stratigraphic horizon. 2. Inderite was not found as pseudomorphs after other borate minerals, or as veins, or with crystallographic orientations common to anything but single inderite crystals. 3. The mineral is apparently a low-temperature form; its synthesis at 35° C (6) and its high content of water of crystallization bear this out.

Ezcurrite differs from minerals of the borax-kernite series ($Na_2O.2B_2O_3.nH_2O$) in having a different molecular Na_2O–B_2O_3 ratio: 2 : 5. It is

perhaps but one mineral of a new sodium borate series ($2Na_2O.5B_2O_3.nH_2O$) that might exist in nature.

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EFFECTS OF RADON IN DRILL HOLES ON GAMMA-RAY LOGS[1]

L. S. HILPERT AND C. M. BUNKER

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ABSTRACT

Drill holes in uranium deposits in the Todilto limestone of Late Jurassic age near Grants, New Mexico, do not yield duplicate gamma-ray logs when probed at different times; some logs show equivalent uranium greatly in excess, in thickness and grade, of the chemical and laboratory radiometric analyses. Radon and its daughter products principally cause the discrepancies. Experimental work was undertaken by the writers to learn the relations of the radon to the uranium deposits and its behavior under different physical conditions. The work is based on the interpretation of about 600 gamma-ray logs, taken from 480 drill holes.

Abnormally high amounts of radon, referred to here as contamination, ranged from barely detectable amounts to amounts that emitted as much radiation as ore-grade material. Most contaminated holes were in the higher-grade ore, and the contamination increased with elapsed time after drilling.

[1] Publication authorized by the Director, U. S. Geological Survey.

Geologic conditions favorable for contamination by radon and its daughter products in drill holes are: proximity to uranium deposits and fractured or highly permeable rocks above the water table. Most drill holes can be decontaminated by blowing them out with compressed air or filling them with water. Water, however, tends to reduce the thickness-times-grade figures below the amounts determined in air.

INTRODUCTION

DURING the fall of 1954, it was necessary for the U. S. Geological Survey to obtain gamma-ray logs of the drill holes on properties being explored under Defense Minerals Exploration Administration assistance near Grants, N. Mex. Early in the work it was found that some of the drill holes did not yield duplicate logs when probed at different times; some showed amounts of equivalent uranium greatly in excess, both in thickness and grade, of the amounts determined chemically or by laboratory radiometric analysis. In fact, the disparity between logs of some holes was so great that the gamma-ray data were very misleading when used alone for determining uranium reserves. This had also been the experience of private companies and individuals in the area, and as a result, such logs were considered unreliable for uranium determinations. It was apparent that if gamma-ray logs were to be used effectively, either by the Government or private industry, to help appraise uranium reserves, the causes for the discrepancies would have to be determined, and the means found to eliminate or control them.

Company personnel, suspecting that the cause might be radon gas and its gamma-emitting daughter products, had used compressed air to blow out the affected holes. Although this practice met with some success, to our knowledge no one had actually identified radon and its gamma-emitting daughters as the cause of the anomalously high and variable gamma-ray intensities, and data were sparse on the specific nature, distribution, and spatial relationships of the radioactive materials causing the radioactivity.

Late in 1954, A. B. Tanner of the U. S. Geological Survey became interested in reports of the relatively high radon content of some of the drill holes in the Grants area. He took air samples from selected holes and specifically identified by alpha-particle measurement the presence of radon in high concentrations. He then did some experimental work to determine the relations of the radon to atmospheric pressure, temperature, and wind conditions. His work showed that the radon concentration increased at times of decreasing atmospheric pressure and was affected by wind conditions (written communication, 1956).

For some of the same holes in which Tanner identified radon in abnormally high concentration, gamma-ray logs—obtained almost simultaneously—showed curves with peaks that agreed in position and intensity with what would be expected from the radon concentrations measured by Tanner. Where gamma-ray logs showed a radiation intensity more than twice background for the rocks above and below the ore zone, the drill hole was inferred to be contaminated by the daughter products of radon.

About 600 gamma-ray logs, taken from 480 drill holes were evaluated by the writers to learn the relation of the radon to the uranium deposits, its be-

havior under different conditions of possible removal by use of compressed air or water, and the degree of contamination. The depth of the drill holes ranged from 30 feet to about 400 feet and averaged about 200 feet. The results are presented here to assist mining men and geologists to obtain more reliable gamma-ray data and better evaluations of such data.

The properties on which the work was done are all in sec. 30, T. 13 N., R. 9 W., McKinley County, N. Mex. (Fig. 1). Sec. 30 is accessible by about 1 mile of graded dirt road that leads westward from State Highway 53

FIG. 1. Index map of northwestern New Mexico showing location of sec. 30, T. 13 N., R. 9 W., N. M. P. M.

about 12 miles north of Grants. The work was done between November 1954 and April 1955 by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

RADON—ITS PROPERTIES AND CHARACTERISTICS

Radon is a gaseous radioelement, a daughter product formed during the natural disintegration of uranium. It emits no significant gamma radiation, so that it is not directly or specifically determined by gamma-ray measurement. It disintegrates, however, to short-lived daughter products that do emit gamma radiation. One of these is bismuth 214, which has a half-life of about 20

minutes. The gamma rays from bismuth 214 are more energetic and more easily detected than the gamma rays from the other uranium daughter products and largely constitute what is registered by hand counters and logging equipment when the radioactivity of uranium ore is measured.

All uraniferous minerals emit some of the radon that is generated within them. Radon is unique among the radioactive daughters of uranium, in that as a gas it can migrate from the parent mineral into air as well as into solution. The more open the lattice of the mineral, the greater will be the loss of radon (1, p. 139).

Radon is many times heavier than any of the major components of air, but because of its very small percentage per unit volume in the atmosphere of a drill hole it shows no tendency to stratify. Its location within the drill hole is affected by the same factors that cause movement of the air, such as atmospheric pressure and surface wind.

It is soluble in water and other hydrogenous fluids. The solubility is affeted by the amount of surface area exposed to the radon; hence, a flat surface of water absorbs less radon than does a froth. For this reason care was taken in filling the holes with water, as described subsequently, for this study.

GENERAL GEOLOGY

Stratigraphy and Structure

The rocks exposed in sec. 30, T. 13 N., R. 9 W., are a conformable sedimentary sequence that includes, from bottom to top, the Entrada sandstone, Todilto limestone, Summerville formation, and what is tentatively called the Bluff sandstone, all of Jurassic age. These rocks dip northward at a low angle, are gently folded, and locally are broken by faults that generally have not more than a few feet of displacement. Most of the surface is covered by a mantle of windblown sand that ranges from a few feet to about 90 feet in thickness. Erosion, prior to the deposition of the sand, locally removed most of the beds above the Todilto limestone and some or all of the Todilto as well.

The uranium deposits in section 30 are in the Todilto limestone, which ranges from a knife edge to about 40 feet in thickness and which averages about 20 feet in thickness. It is a dense medium- to dark-gray fetid limestone that weathers white. It generally is laminated and has thin siltstone layers, along which it parts into slabby beds that range from 1 inch to 6 inches in thickness. It is abundantly fractured and jointed.

The Todilto lies on the Entrada sandstone, which is a reddish-orange fine-grained crossbedded sandstone, about 150 feet in thickness. Although the contact is gradational, it can be located readily within a stratigraphic interval of less than a foot.

Overlying the Todilto limestone is the Summerville formation. It is a soft fine-grained locally argillaceous sandstone that occurs as alternating dark-reddish-brown and pale-orange-yellow beds, each a few feet thick. It has an average thickness of about 150 feet. The contact between the Todilto and Summerville is gradational, and, locally, interfingering of the limestone and sandstone adds to the difficulty of establishing a precise contact. The Bluff

sandstone overlies the Summerville and is a pale-yellowish-brown fine- to medium-grained crossbedded sandstone. In the general vicinity of section 30 it is about 150 feet thick. In sec. 30 the upper part has been removed leaving a maximum thickness of about 100 feet.

Uranium Deposits

The uranium deposits in the Todilto limestone are irregular elongate units, as shown in Figure 2. They are roughly tabular and consist of concentrations of massive uraninite and the secondary yellow minerals tyuyamunite, meta-tyuyamunite, uranophane, and some carnotite, along with a gangue of pyrite and some barite and fluorite. Uraninite is distributed along the bedding as

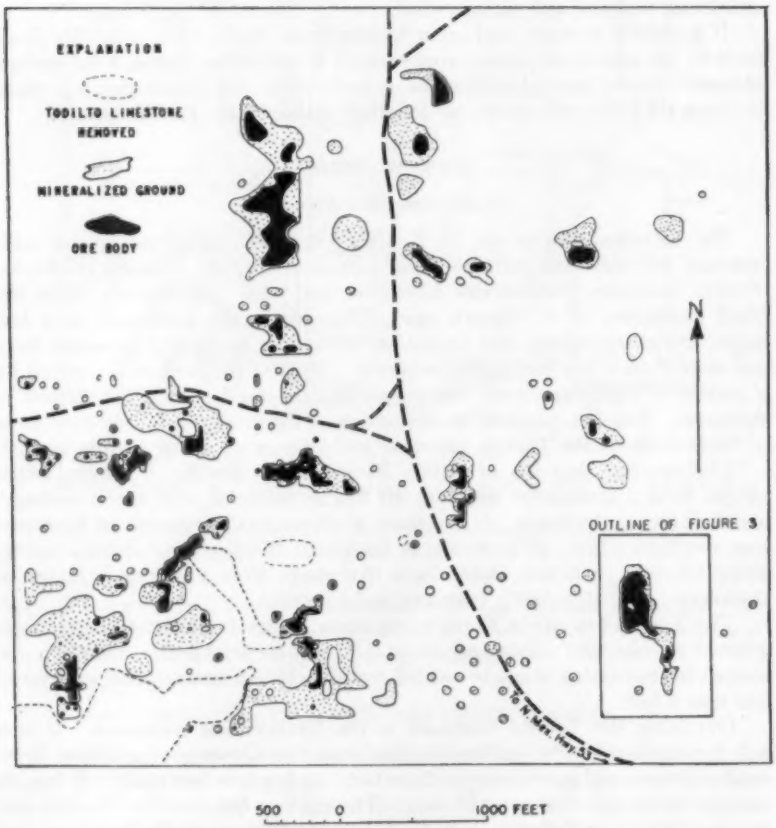

FIG. 2. Map of sec. 30, T. 13 N., R. 9 W., N. M. P. M., showing the known uranium deposits and outline of Figure 3.

irregular seams and disseminated masses. The yellow minerals occur along the joints, fractures, and other open spaces in the limestone.

In sec. 30 uranium deposits (defined as material having a cutoff of 0.01 percent U_3O_8) range from masses with dimensions of only a few feet to masses as much as 500 feet wide, 1,200 feet long, and 40 feet thick. They probably average about 200 feet in width, 500 feet in length, and 20 feet in thickness. Within the deposits the ore bodies (defined as material with cutoffs of 0.10 percent U_3O_8 and 1 foot in thickness) range from masses with dimensions of only a few feet to masses as much as 250 feet wide, 650 feet long, and 20 feet thick. They average about 100 feet wide, 200 feet long, and 6 feet thick. The ore averages about 0.30 percent U_3O_8. Individual deposits may contain one or more ore bodies.

The deposits in the Todilto limestone occur along anticlinal folds that generally include the lower part of the Summerville formation and, locally, the upper part of the Entrada sandstone. Generally, the deposits have a northerly or easterly trend and locally occur in clusters, where the individual folds are roughly parallel. Individual folds may be only a few feet or more than 100 feet long; their relief ranges from less than 1 foot to about 5 feet. Along the folds the limestone is thicker and more intensely fractured and jointed than away from them, and the thickening has developed mostly in the upper part. The principal joints are parallel to the long axes of the folds. A less well developed set of joints trends roughly normal to the fold axes.

In most deposits the ore is near the base of the Todilto limestone, but in some it occurs in the middle of upper parts and, in a few, it "makes" throughout most of the limestone interval, even extending into the basal part of the overlying Summerville formation. The ore is thicker and higher in grade along the axes of the folds, and it feathers out along the flanks. The ore bodies generally are larger where there are several associated folds.

DRILLING METHODS

It has been the general practice in sec. 30, T. 13 N., R. 9 W., and in the Grants area as a whole, to do exploratory and development drilling in the Todilto limestone with rotary-type drill rigs, using a tricone-type plug bit. The bit size most commonly employed is 4 inches in diameter and drills a hole 4¼ inches in diameter. To avoid casing the holes, the upper part through the windblown sand is drilled with water, and the lower part, through the lower Summerville and Todilto limestone, is drilled with compressed air. Use of compressed air as the drilling medium is quite effective in sec. 30 because the rocks in the ore zone lie above the water table.

SAMPLING METHODS

As with drilling, sampling of the Todilto limestone in sec. 30, and in the Grants area as a whole, follows a general pattern. Samples of the drill cuttings are collected from each 2-foot run in a cyclone-type sample collector at the hole collar. When a sample shows the presence of uranium minerals or is determined by a conventional gamma counter to have anomalous radioactivity

above a specified cutoff, it is packaged for assay. The assay is determined chemically or radiometrically. Radiometric assays generally are determined by a laboratory scaler.

The drill holes are also probed with a gamma-ray counting instrument, generally of the Geiger-Müller type. Most of these are hand-portable, having a hand-operated reel and a depth indicator. With these instruments the probe (Geiger tube) is lowered and raised through the hole manually, and the radioactivity is measured at convenient intervals within the hole, generally every foot, but in some holes every half a foot through mineralized zones. The resultant gamma-ray log of the hole commonly provides supplementary data to what is detected in the drill cuttings and assists in selecting samples of the drill cuttings for assay. Oftentimes, however, the gamma-ray data are used alone to measure the thickness and grade of uraniferous material.

WORK PLAN AND EQUIPMENT USED

Work Plan

The area of sec. 30, T. 13 N., R. 9 W., was selected for the experimental work because considerable geologic information was available on the distribution and habits of ore bodies, and because exploration then in progress provided a large number of drill holes and allowed some control over the time intervals between completion of drilling and the logging of drill holes.

The experimental work was planned to determine the distribution and degree of contamination in drill holes, and to test methods of reducing such contamination. To determine the spatial distribution of contaminated drill holes in relation to the distance from deposits and their grade, gamma-ray logs were obtained from 480 drill holes. To determine the degree of contamination as a function of time elapsed after completion of drilling, repeated gamma-ray logs were made in selected drill holes at various time intervals after drilling had been completed.

Two methods of reducing drill-hole contamination caused by the daughter products of radon were tested: (1) blowing out the hole with compressed air for various periods of time, and (2) displacing the air column in the hole with water.

Gamma-ray Logging Equipment and Procedures

The gamma-ray logging equipment used is of the Geiger-Müller type. The equipment is truck mounted and consists of five major components: a 115-volt AC power plant, a reel unit to lower and raise the probe in a drill hole, a $\frac{3}{4}$-inch (outside diameter) waterproof brass probe containing a $7\frac{1}{4}$-inch long Geiger-Müller tube, a ratemeter-amplifier that amplifies and indicates the number of electrical impulses received through the cable from the detector tube, and a strip-chart recorder, which graphically plots the number of impulses received by the ratemeter versus probe depth in the hole.

The equipment is operated by one man. Before and after logging each hole

the operator checks the equipment with calibrated radioactive standards to maintain proper performance and response. The probe is lowered to the bottom of the drill hole and the hole is logged as the probe is withdrawn at a rate of 5 feet per minute. The variation in the quantity of gamma-radiation incident on the probe is recorded by the strip-chart recorder.

Before this study the logging equipment was calibrated to determine the thickness and grade of radioactive layers of uraniferous material. Simulated ore bodies of predetermined grade and thickness were constructed in 4-foot diameter culverts having in the center a 2-inch diameter $\frac{1}{64}$-inch-thick aluminum casing. Data obtained from these simulated ore bodies were used to construct graphs showing the relationship of grade, thickness, and count rate. The graphs are used to interpret, in terms of percent U_3O_8 and thickness, the strip charts obtained from exploratory drill holes.

Water and Air Equipment

A 500-gallon water truck and a tractor-mounted air compressor with a rated capacity of 105 cubic feet per minute were made available to the project by the U. S. Atomic Energy Commission. The compressor was set to operate at 60 pounds air pressure. Installed on the front of the tractor was a reel with 500 feet of $\frac{3}{4}$-inch air hose that could be manually lowered or raised in a drill hole. Secured to the lower end of the hose was a 10-foot section of $\frac{1}{2}$-inch (inside diameter) steel pipe, which served to guide the hose into the hole and prevented the end of the hose from whipping when air was forced through it. At the upper end of the hose a coupling was installed that matched either the fitting on the air receiver of the compressor or the fitting on the tank of the water truck, permitting prompt use of the reel-and-hose assembly for either air or water. A fitting was also installed at the top of the water tank so it could be attached to the compressor to increase the rate of discharge of water from the tank to the drill hole.

Water was added to the holes by lowering the hose to the bottom of the hole before releasing the water from the tank. This method prevented material from being washed down the sides of the hole and helped to reduce turbulence and frothing, which affect the solubility of radon in water. After sufficient water was added to cover the ore zone the hose was withdrawn and the hole was gamma-ray logged.

IDENTIFICATION OF "SALTED" HOLES

In some holes the cuttings from high-grade layers have a tendency to stick to the walls of the hole above the ore zone, forming what is generally referred to as a "salted" hole. A "salted" hole gives a gamma-ray log curve that tapers off rather abruptly immediately above a high-grade ore layer or shows a rather pronounced anomaly above the ore zone where the mineralized cuttings collect next to a rock projection or damp zone in the hole. No salted holes were recognized in sec. 30, and the chances of confusing them with radon-contaminated holes is considered unlikely.

RESULTS

Relations of Contamination to Grade and to Elapsed Time After Drilling

Evaluation of gamma-ray logs from the 480 drill holes revealed that 102, or 21 percent, of the holes were contaminated. These data are listed in Table 1, which shows a higher proportion of contaminated holes in the higher grade classes and an increasing number of contaminated holes as the time between drilling and logging increases. If all holes had been logged more than 24 hours after drilling, it is likely the number of contaminated holes would have been considerably greater than 102.

TABLE 1

NUMBERS OF HOLES LOGGED AND THE NUMBER AND PERCENTAGE FOUND TO BE CONTAMINATED, RELATIVE TO GRADE AND THE ELAPSED TIME OF LOGGING AFTER DRILLING

Elapsed time after drilling	Number of holes logged, and number and percent contaminated											
	Grade cutoffs									Totals by elapsed time brackets		
	<0.01 pct. U_3O_8 or <0.02 pct. eU_3O_8[1]			0.01 to 0.099 pct. U_3O_8 or 0.02 to 0.149 pct. eU_3O_8[1]			0.10 pct. or more U_3O_8 or 0.15 pct. or more eU_3O_8[1]					
	Logged	Contaminated		Logged	Contaminated		Logged	Contaminated		Logged	Contaminated	
	No.	No.	Pct.	No.	No.	Pct.	No.	No.	Pct.	No.	No.	Pct.
<1 hour	68	1	1	41	2	5	71	3	4	180	6	3
1–24 hours	55	2	4	42	11	26	40	10	25	137	23	17
>24 hours	68	9	13	43	19	44	52	45	87	163	73	45
Totals and averages of totals by grade brackets	191	12	6	126	32	25	163	58	36	480	102	21

[1] Note: eU_3O_8 cutoffs refer only to inhole gamma-ray data.

Chemical assays and laboratory radiometric assays of the drill cuttings were available for comparison with the inhole gamma-ray data for many drill holes. Chemical data were used in classifying holes as to grade (Table 1) when available and when sample recovery was considered reliable. Laboratory radiometric data showed good correlation with the chemical assays and were used when chemical data were not available. Inhole gamma-ray data, although corrected and reduced by the recognizable amounts of radon contamination, generally showed thickness-times-grade figures about 50 percent higher than the chemical figures. When no chemical or laboratory radiometric data were available, or were considered unreliable, the inhole gamma-ray data were used. The equivalent U_3O_8 cutoffs in Table 1 refer only to inhole gamma-ray data. The higher cutoffs for these data were selected to be

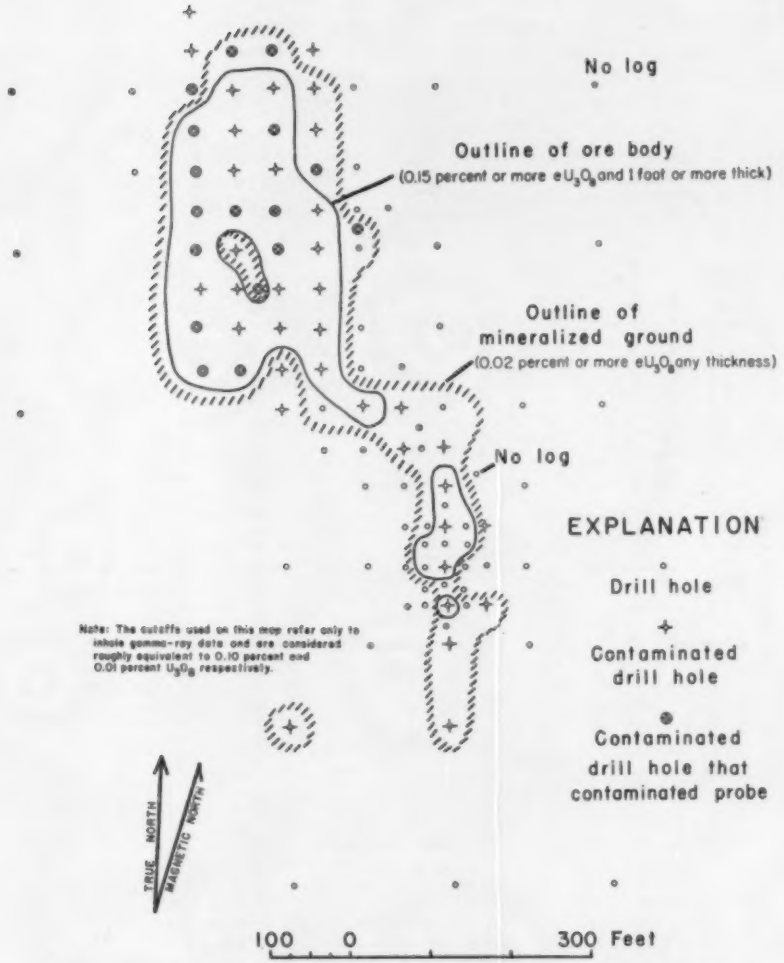
No log
Outline of ore body
(0.15 percent or more eU_3O_8 and 1 foot or more thick)
Outline of mineralized ground
(0.02 percent or more eU_3O_8 any thickness)
No log
EXPLANATION
Drill hole
Contaminated drill hole
Contaminated drill hole that contaminated probe
Note: The cutoffs used on this map refer only to inhole gamma-ray data and are considered roughly equivalent to 0.10 percent and 0.01 percent U_3O_8 respectively.
TRUE NORTH
MAGNETIC NORTH
100 0 300 Feet

FIG. 3. Map showing the relations of radon-contaminated drill holes to a uranium deposit.

roughly comparable to the cutoffs used for the chemical and laboratory radiometric data.

In addition to the influence of grade and time on contamination in drill holes, there is also a spatial relation to ore deposits. Most complete logging coverage was obtained for the deposit shown in Figure 3. Of the holes shown within the mineralized area, 75 percent were contaminated. Nearly all

of these contaminated holes were logged several days after they were drilled, whereas all but one of the uncontaminated holes were logged within an hour of drilling. Outside of the mineralized area only seven holes showed contamination. One of these was logged within an hour after it was drilled; the other six were logged two weeks or more after drilling. It seems note-

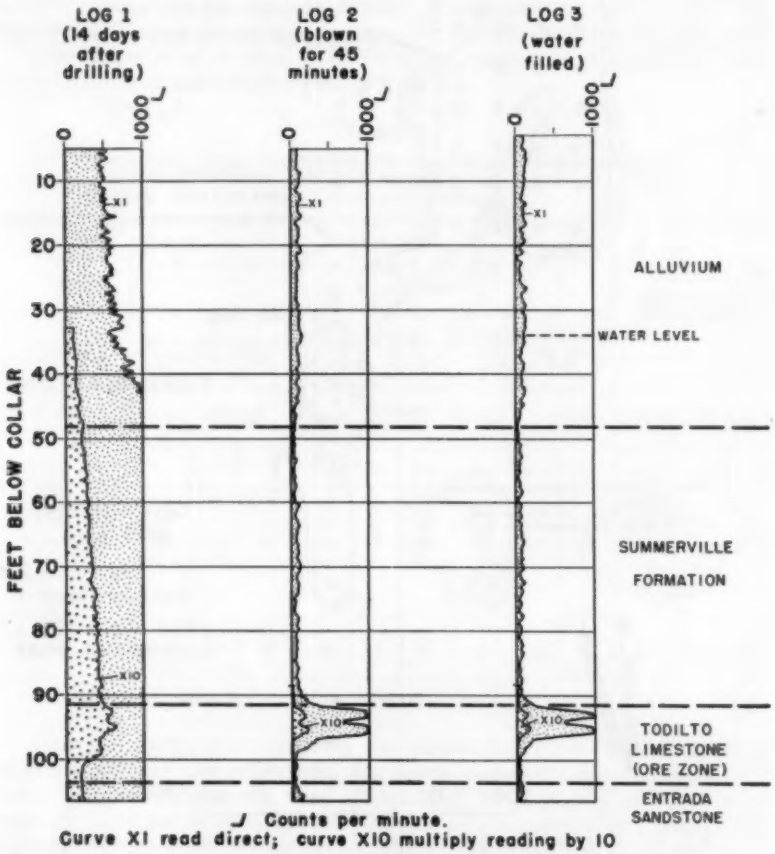

FIG. 4. Three gamma-ray logs of hole J-9.5 showing extreme radon contamination, and effects of blowing out hole with air and filling hole with water.

worthy that none of these seven contaminated holes is farther than about 50 feet from known mineralized ground.

Probe-contaminating holes are shown in Figure 3. This contamination was caused by the deposition on the probe of solid short-lived gamma-emitting daughter products of the radon. It resulted in a count rate above normal

background when the probe was removed from the drill hole and an abnormally high count rate when the probe was checked against calibrated radioactive standards. In general, these holes showed the highest radon concentration, and all are in or near the largest ore body (Fig. 3).

Degree of Contamination

The degree of contamination of the drill holes ranged from barely detectable amounts on the logs to amounts that gave count rates as high as those

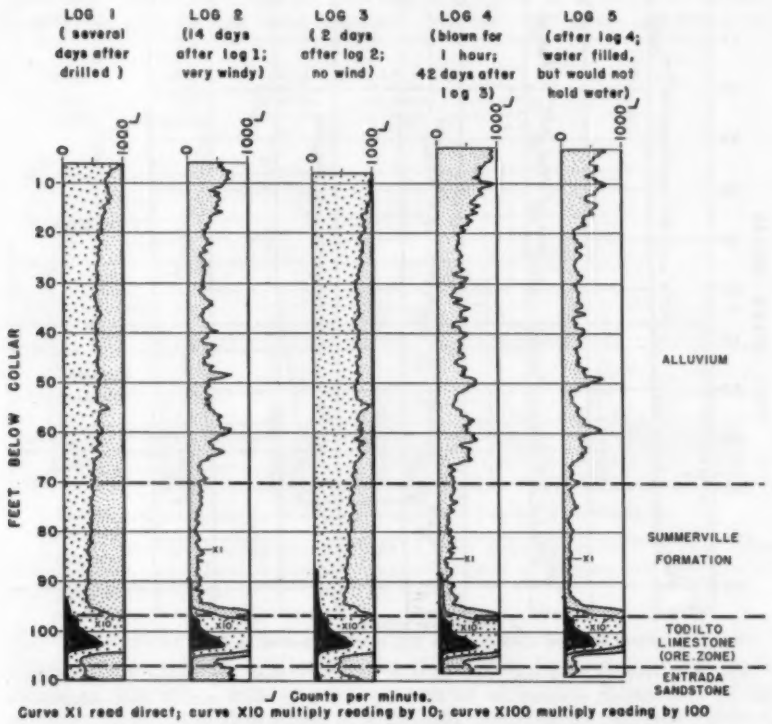

FIG. 5. Five gamma-ray logs of hole J-10 showing effects of a windy day on radon contamination and of blowing out hole with air and filling hole with water.

given off by ore-grade material. Figure 4, log 1, illustrates a contaminated hole. This log shows a count range from about 6,500 counts per minute in the ore zone to 500 counts per minute at the hole collar. Between the depths of 75 and 100 feet below the collar, or through a thickness of 25 feet, the count rate converted to equivalent uranium is in the grade range from 0.1 to 0.2

percent. Log 2, taken after the hole was blown out with compressed air, shows a peak of about 2,000 counts per minute for a thickness of about 2 feet. This is about equivalent to 0.05 percent uranium.

Figure 5 shows examples of an extremely contaminated hole. Log 3, for example, shows the lowest count, about 5,000 counts per minute, immediately above the ore zone. It increases upward in the hole through the barren Summerville formation and alluvium to about 10,000 counts per minute at the

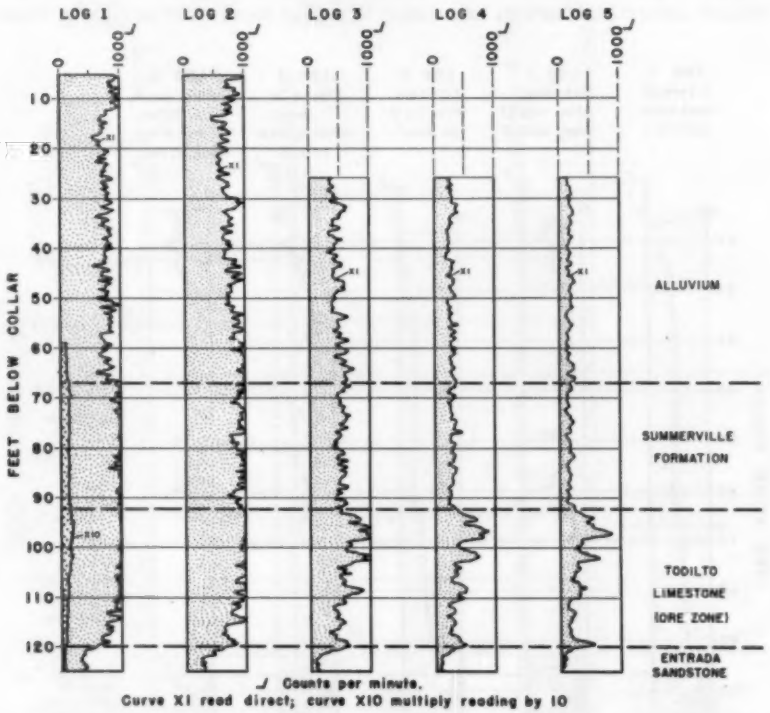

FIG. 6. Five gamma-ray logs of hole H.5–9.75 showing radon contamination and its progressive elimination by blowing out hole with air in four successive 15-minute intervals. Log 1 taken 18 hours after hole was drilled.

hole collar. Converted to equivalent uranium this log would indicate more than 100 feet of material with a grade that ranged from several percent in the ore zone to about 0.3 percent at the hole collar. Actually, this hole contained about 7 feet of ore that averaged 1.0 percent eU_3O_8, as interpreted from gamma-ray log 2. Chemical assay of the cuttings showed 10 feet of ore that averaged 0.55 percent U_3O_8.

Eliminating Contamination

After the initial logs were taken, the more highly contaminated holes were blown out with compressed air for periods that ranged from 15 minutes to 2 hours, to find if the holes could be decontaminated, and, if so, how long it would take. In general, most holes could be decontaminated by blowing them out for about 30 minutes; a few extremely contaminated holes, however, required 1 to 2 hours.

Log 1 of Figure 6 shows moderate radon contamination in a hole logged 18 hours after it was drilled. After this log was taken the hole was blown out in four successive 15-minute intervals, and logs 2, 3, 4, and 5 were taken immediately after each of these intervals. For the rocks above and below the

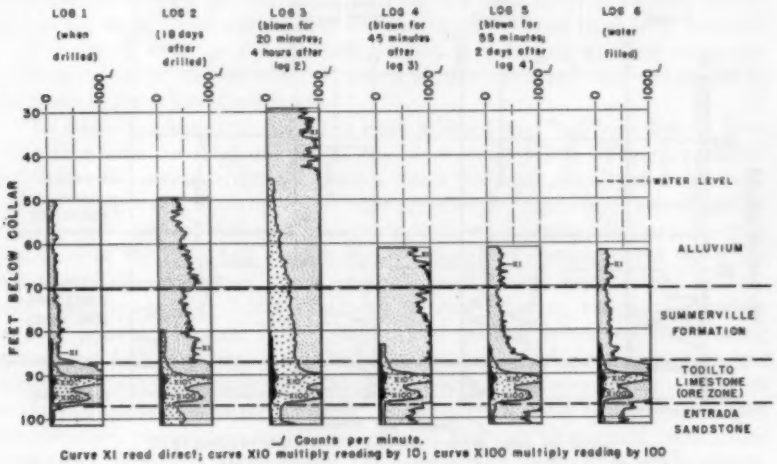
LOG 1 (when drilled)
LOG 2 (18 days after drilled)
LOG 3 (blown for 20 minutes; 4 hours after log 2)
LOG 4 (blown for 45 minutes after log 3)
LOG 5 (blown for 55 minutes; 2 days after log 4)
LOG 6 (water filled)
FEET BELOW COLLAR
WATER LEVEL
ALLUVIUM
SUMMERVILLE FORMATION
TODILTO LIMESTONE (ORE ZONE)
ENTRADA SANDSTONE
Counts per minute.
Curve XI read direct; curve X10 multiply reading by 10; curve X100 multiply reading by 100

FIG. 7. Six gamma-ray logs of hole J.5–8.5 showing radon-free hole when drilled, radon contamination after 18 days, and effects of blowing out hole with air and filling hole with water.

Todilto limestone the count rate on log 5 is near the normal background. These logs were taken to illustrate the response of the contamination to the period of blowing. Actually one continuous 30-minute period of blowing probably would have cleared the hole, as the contamination may have built up between logging setups. After blowing out the hole it required about 5 to 10 minutes to remove the equipment and get the logging instrument in position to start logging. The logging time was about 30 minutes for each log. The entire operation took 3¼ hours.

A few holes were not readily decontaminated by blowing. Log 2 of Figure 7 shows a contaminated hole 18 days after it was drilled; log 1 was taken immediately after it was drilled. Four hours after log 2 was taken the hole was blown out for 20 minutes and then relogged (log 3). On this log

much greater contamination is indicated. Log 4 shows some decontamination after the hole was blown out for an additional 45 minutes, but the contamination still shows at least 1,000 counts per minute above the normal background. An additional 55-minute period of blowing reduced the contamination to near background above the ore zone, but a significant amount still remained in the hole below the ore zone.

Log 3 of Figure 8 is another example of contamination that was not reduced materially after an hour of blowing. In the upper part of the hole the count was actually higher. Log 4 of Figure 8 illustrates how water reduces contamination that is not materially affected by blowing. Immediately after

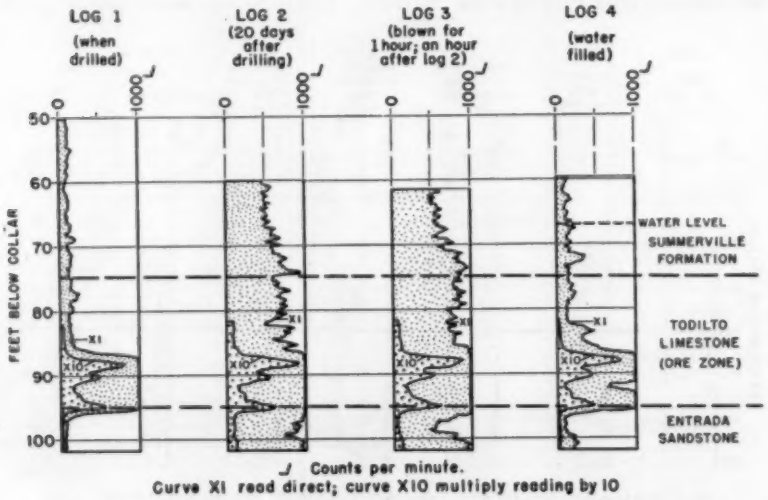

FIG. 8. Four gamma-ray logs of hole J.5–8 showing radon-free hole when drilled, radon contamination after 3-week period, and effects of blowing out hole with air and by filling hole with water.

log 3 was taken the hole was filled with water and log 4 was taken. Log 4 shows the contamination reduced to near background, as shown on log 1.

Effects of Water on Count Rate and Apparent Thickness of Material

The data presented below cannot be directly compared with data from other areas because of varying physical conditions. For example, variations in the distance between the probe and hole wall and, equivalent in effect, variations in hole diameter within drill holes or among a group of drill holes will alter the results. Drilling fluid, of a density different from water, remaining in the hole will also affect the results.

Although filling a drill hole with water tended to decontaminate it, it also reduced the count rate and the indicated thickness of the individual mineralized

layers to less than that obtained in air. Log 6 of Figure 7 and log 4 of Figure 8 show some reduction below the peak count rates of the respective peaks shown on log 1. Some contamination remaining in these holes before and after they were filled with water, however, hides the general relation somewhat. Log 2 of Figure 4 shows a hole that is uncontaminated. Log 3 shows it after it was filled with water. The peak counts in the ore zone have been reduced and the thickness of the anomalies has been reduced slightly.

Many holes would not hold water throughout the logging. Even so, the contamination was generally reduced, and the count rate as well as the indicated thickness of the individual mineralized layers fell to less than pre-contamination levels in some holes. Log 5 of Figure 5 is an example. Although the small scale of the illustrations makes it difficult to compare the thickness relations, it can readily be seen that the peak count in the ore zone as well as the background count above and below the ore zone have been reduced.

The use of water as a decontaminant and as a drilling medium raises the question: what is the net effect of water on the count rate and the apparent thickness of the mineralized layers?

To make a comparison, 13 holes were selected that had been logged both when they were air filled and when they were water filled. The rocks above and below the ore zone did not show a count that was more than twice their normal background of about 100 counts per minute, either before or after the holes were blown out with compressed air, thus providing reasonable assurance that none of the holes had any significant amount of contamination when the logs were taken. Sample thicknesses and peak counts were determined for each anomaly showing 1,000 counts per minute, or more, roughly equivalent to 0.02 percent or more U_3O_8. Under the present system of interpreting gamma-ray logs in terms of the thickness and grade (eU_3O_8) of a layer, the thickness of a layer is determined to be the width of the anomaly at two-thirds of the peak deflection of the anomaly. Counts per minute have been retained for statistical purposes to avoid some loss of accuracy that would result from converting the counts to equivalent U_3O_8, especially in the high grade ranges.

Table 2 compares the apparent thickness and grade relations of water-filled versus air-filled holes. For individual holes, apparent thickness differences between water and air of about 5 percent or less are probably not significant. For several holes the totals are more significant. The total apparent sample thickness for the 13 holes shows a difference of about 14 feet between air-filled and water-filled holes, which is about 15 percent. Of the 13 holes, 9 show a reduced sample thickness for water versus air. Of the 4 that show an inverse relationship, only 2 show a difference great enough to be significant. These two, holes J.5–10.5 and T–20.25, both produced rather complex log curves, and it is probable that these inverse thickness relations reflect a difference in interpretation of the respective logs.

The thickness-times-peak figures of Table 2, which actually are measures of the total material in the sample, afford a significant comparison of gamma-ray data taken in water and air-filled holes. In Table 2 the figures represent the total for all samples for each hole that make the specified cutoff of 1,000 counts per minute. The table shows that the figure for each of the 13 holes is

less in water than in air, and the differences range from 11 to 29 percent. The difference for the total of the 13 holes is 22 percent. From these figures it can be expected that gamma-ray logs taken in water-filled holes of about 4 inches in diameter, and using a $\frac{7}{8}$-inch logging probe, will produce readings that will range from about 10 to 30 percent below the readings taken in air and will average about 20 percent less.

In order to show the counterpart of the sample thickness relations, the weighted arithmetic mean counts per minute (grade of the hole in counts per minute) are listed in Table 2 for each drill hole. Of the 13 holes logged, 10 show a reduced mean count in water. The other 3 show an increased count. Those that show an increased mean count in water also show a marked reduction in apparent sample thickness. The average weighted arithmetic mean

TABLE 2

A COMPARISON OF SAMPLE THICKNESS AND GRADE RELATIONS, IN COUNTS PER MINUTE, OF 13 AIR-FILLED VERSUS WATER-FILLED HOLES, AS INTERPRETED FROM GAMMA-RAY LOGS

Drill-hole number	Air-filled holes			Water-filled holes			Percentage differences of water-filled versus air-filled holes		
	Sample thickness (feet)	Sample thickness (feet) times peak counts/min	Weighted arithmetic mean counts/min	Sample thickness (feet)	Sample thickness (feet) times peak counts/min	Weighted arithmetic mean counts/min	Sample thickness (feet)	Sample thickness (feet) times peak counts/min	Weighted arithmetic mean counts/min
J.5–8	7.7	28,500	3,700	6.0	23,500	3,900	−22	−18	+5
J.5–9	8.3	101,500	12,200	7.1	86,000	12,100	−14	−15	−1
J-9.5	2.0	4,000	2,000	1.8	3,000	1,700	−10	−25	−15
J.5–9.5	7.0	146,000	20,800	6.1	104,500	17,100	−13	−28	−18
J.5–10	6.6	185,000	28,000	5.9	157,500	26,700	−11	−15	−5
J-10.5	5.4	96,500	17,900	4.5	76,000	16,900	−17	−21	−6
J.5–10.5	5.9	121,500	20,600	7.0	100,500	14,400	+19	−17	−30
J.5–11	8.6	91,000	10,600	3.5	65,000	18,600	−60	−29	+75
S.5–21.75	3.3	9,500	2,900	3.4	8,500	2,500	+3	−11	−14
S.75–18.75	16.6	261,500	15,800	12.2	200,000	16,400	−27	−24	+4
T-19	11.9	205,500	17,300	10.6	149,500	14,100	−6	−27	−18
T-19.25	8.2	145,000	17,700	8.4	114,000	13,600	+2	−21	−23
T-20.25	4.2	71,500	17,000	4.8	56,500	11,800	+14	−21	−31
Totals and averages of totals	95.7	1,467,000	15,300	81.3	1,144,500	14,100	−15	−22	−8

counts per minute for the 13 holes in water is 8 percent less than in air. The table shows that the rather wide variations in the percentage differences between individual holes is not significant, as they are compensated for by the sample thicknesses within each hole. Therefore, the figure of sample thickness times peak counts per minute is the most significant.

CONCLUSIONS

Geologic conditions favorable for contamination by radon and its daughter products in drill holes are: proximity to uranium deposits, and fractured or highly permeable rocks above the water table. Contamination should be suspected where:

1. Gamma-ray logs indicate higher grade (equivalent U_3O_8) and greater thickness of a radioactive layer than is indicated by chemical and radiometric analyses of drill cuttings or core samples.

2. Gamma-ray logs show a radiation intensity significantly higher than background for the barren rocks above and below the ore zone.

3. Gamma-ray logs taken at different times from the same drill hole show rather wide variation in radiation intensity.

4. The probe of the logging equipment, when removed from the drill hole, gives an abnormally high counting rate, which decreases to normal after 2 to 3 hours.

Radon has contaminated drill holes in sec. 30, T. 13 N., R. 9 W., because of the fractured nature of the Todilto limestone, which provides passageways for the radon to migrate in air currents away from the parent-mineral faces to the drill holes, and because the ore zone lies above the water table.

Most drill holes can be decontaminated by blowing them out with compressed air for about 30 minutes. Some of the more highly contaminated holes require blowing for an hour or more. They might be decontaminated more effectively by evacuating the air. Filling holes with water also appears to be an effective means of decontaminating them, although more tests should be made to find out if consistent results can be expected.

On the basis of a comparison of the logs taken in air and water, respectively, from 13 selected holes, it was found that water reduced the total thickness-times-grade figures by about 20 percent. This effect, however, cannot be directly compared with similar effects in other areas because of varying physical conditions.

To avoid most contamination effects holes should be logged immediately after they are drilled.

ACKNOWLEDGMENTS

The excellent cooperation of the mining companies greatly expedited the work, particularly the Four Corners Exploration Co., Holly Minerals Corp., All States Uranium Co., Flat Top Mining Co., and Mid-Continent Uranium Corp., on whose properties the work was done. The writers are grateful for the continuing interest and assistance of F. O. Manol, Irving Rapaport, Paul Melancon, and Joe McCormick for providing necessary maps, assay data, drill logs, and the extra effort required to obtain factual drilling information. Thanks are also due the staff of the Exploration Division, Grand Junction Operations Office, U. S. Atomic Energy Commission, for their assistance in providing a water truck and air compressor.

The work was done by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

U. S. GEOLOGICAL SURVEY,
GRAND JUNCTION AND DENVER, COLO.,
Jan. 24, 1957

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SCIENTIFIC COMMUNICATIONS

A POSSIBLE ORIGIN OF NATIVE COPPER

G. VIBERT DOUGLAS AND G. D. THOMAS

Deposits of native copper are known in various parts of the world and have been described by many authors. The general texts on mineral deposits by Lindgren (1928), Bateman (1950), Raguin (1949), and others, list these occurrences.

The origin of native copper has been the subject of many papers some of which are published in the bibliography at the end of this paper.

Cornwall (1956) has made a comprehensive study of the literature on native copper, listing the theories that attempt to explain the deposition of native copper in lavas and as a constituent of clastic sedimentary rocks such as are found at Keweenaw Point and the White Pine mine, Michigan, U. S. A.

The theories of Graton, Butler, Broderick, Van Hise and Smyth have been outlined in the experiments of R. C. Wells (1925), giving the following equations:

$$Cu_2S + 5\,Fe_2O_3 + 11\,H_2SO_4 \rightleftharpoons 10\,FeSO_4 + 2\,CuSO_4 + 11\,H_2O$$

$$Cu_2S + 8\,CuSO_4 + 4\,H_2O = 5\,Cu_2SO_4 + 4\,H_2SO_4$$

$$Cu_2S + 3\,Fe_2O_3 + 5\,H_2SO_4 = 2\,Cu + 6\,FeSO_4 + 5\,H_2O$$

Lindgren (1928) explains the presence of native copper by the action of ferrous sulfate on cuprite, the native copper being formed in weathering zones by the oxidation of chalcocite deposits.

$$Cu_2O + 2\,FeSO_4 + H_2SO_4 = Cu + Fe_2(SO_4)_3 + H_2O$$

$$Cu_2S + 3\,Fe_2(SO_4)_3 + 4\,H_2O = Cu + 6\,FeSO_4 + 4\,H_2O.$$

Recently the senior author visited Keweenaw Point district and the White Pine mine where he collected samples. The native copper is found in amygdaloidal lavas, conglomerates, clastic sedimentary rocks, and very noticeably in fracture planes and joints.

It was learned that methane had been detected at the lower levels, furthermore Levorson (1954) states that disseminated solid bitumen has been found in the same copper bearing series.

It is suggested that methane (or a more complicated organic compound) reacts at a low energy level to give carbon. The following reactions are believed to have taken place.

1. $CuS + 2\,O_2 \rightarrow CuSO_4$
2. $CH_4 + O_2 \rightarrow C + 2\,H_2O$
3. $CuSO_4 + C \rightarrow Cu + SO_2 + CO_2$.

The second equation is the well-known reaction for the production of carbon black. Taking the heats of reaction of the last equation we find that it is endothermic at 25° C.

$$C + O_2 \rightarrow CO_2 + 94.05 \text{ K cal}$$
$$S + O_2 \rightarrow SO_2 + 75.05 \text{ K cal}$$
$$Cu + S + 2\,O_2 \rightarrow CuSO_4 + 178 \text{ K cal}$$

Therefore to make the equation

$$CuSO_4 + C \rightleftharpoons Cu + SO_2 + CO_2$$

go to the right it will require a source of heat greater than 9 K cal/mole. This source of heat must come from the underlying rocks. In the specific case of Keweenaw Point, the Duluth gabbro or volcanics are invoked. In areas such as Cap d'Or, Nova Scotia, or Seal Lake, Labrador, the heat source could be from the cooling lavas.

The present authors, therefore, suggest the following sequence of events in the deposition of native copper in Michigan.

1. Mineralization of the host rock by hypogene epigenetic processes. These processes were responsible for the introduction of copper sulfides.
2. Secondary sulfide enrichment which produced chalcocite and covellite.
3. (Which may have been contemporaneous with 2)—A reaction between $CuSO_4$ and carbon according to the equations given above.

ACKNOWLEDGMENTS

Dr. J. J. Fritts at White Pine and Dr. A. W. Schillinger of Calumet were both most helpful.

DALHOUSIE UNIVERSITY,
HALIFAX, NOVA SCOTIA,
March 6, 1957

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DISCUSSIONS

GENESIS OF NICKEL DEPOSITS, S.W. BRITISH COLUMBIA

Sir: Harald Bjørlykke of Oslo, Norway, has drawn my attention to a paper of his in *Norges Geologiske Undersökelse,* Nr. 168b, 1947, in which he describes the Flåt Mine of Norway. This paper, which escaped my attention for some reason, describes many characteristics of this nickel deposit which are striking in similarity to those of many such nickel deposits referred to for purposes of comparison in my paper on Pacific Nickel (ECON. GEOL., v. 51, no. 5, p. 444–481). Particularly notable are the similarities of almost pipe-like flattened shape, steep attitude, structural position near lenses of gneiss, schlieren and breccias with gradational contacts, higher proportion of copper to nickel in poorer ore, and other minor features.

VANCOUVER, B. C.,
Feb. 15, 1957

A. E. AHO

FACIES RELATIONS IN THE GUNFLINT IRON FORMATION

Sir: In vol. 51, p. 565–595, of this journal, A. M. Goodwin presented a stimulating paper on facies relations in the Gunflint iron formation, making a suggestion that volcanism provided a steady source of iron and silica-bearing solutions and induced cyclical fluctuations in the basin of deposition.

Goodwin suggests that the weathering source of iron and silica does not appear to apply to the Gunflint formation because of complete lack of maturely weathered residual material in the area. In his paper, however (p. 570) he says that locally, the upper few inches of granite and greenstone underlying the basal conglomerate of the Gunflint formation are mildly decomposed. It seems more probably that the deposition of conglomerate was accompanied by extensive wave action, whereby the weathered part of the underlying rocks was easily eroded and carried away into deeper parts of the basin. It seems that there is no reason at all for excluding the factor of chemical weathering during Gunflint time.

The author suggests that the difficulty of transporting ferric iron in surface waters to the site of deposition, followed by reduction to the ferrous state without the aid of organic matter, supports his exclusion of weathering as the source of iron and silica. It seems, however, that the quantitative absence of organic matter in a sediment should not be considered as evidence of its absence during the process of sedimentation. During the process of diagenesis the organic matter is the major reducing agent and may be absent in the rock

because it has been completely oxidized to CO_2 during the early diagenesis. According to Gulyaeva (5), 0.1 gram of organic carbon reduces 0.67 gram of Fe_2O_3 to 0.97 gram of siderite. Relic carbon would be present in the sediment if all iron were reduced. The presence of pyrite and carbonaceous matter (p. 573–575) indicates extreme reducing conditions in presence of abundant organic matter which may represent regenerated humic acids (2). The granules of taconite consist of greenalite in the internal part and of magnetite and hematite in the external part, with hematite in the outer rim. This sequence may be explained by the decreasing amount of organic matter during diagenesis and the growth of granules.

Considering the volcanic source of iron and silica, one should query whether this source would be able to furnish enough material for the deposition of formations occupying a basin measuring 110 miles in length. Hot springs which discharge solutions carrying ferrous iron into a basin would contribute to the formation of a ferruginous deposit immediately near the spring (11). The ferrous iron could not remain in the reduced state after contact with sea water, because the Eh and pH range of volcanic solutions would change abruptly and cause an immediate precipitation of the solute. Behrend (4) describes the submarine spring related to the Santorin volcano. This spring yields warm water which, according to physical laws, rises to the surface of the cooler sea water where it forms a zone of less than a foot in depth, 150 feet in width, and is due to a current 4–5 miles in length. This zone is distinctly visible because of its reddish color due to oxidation of ferrous iron and flocculation of ferric hydroxide. Behrend suggests that ferric hydroxide would form in this case a long irregular ore body. Nowadays some iron is derived also from volcanic sources and deposited together with arenites and alevrites in the Sea of Okhotsk along the island arch of the Kuriles and the Kamchatka Peninsula (8). This iron is deposited close to the shore and its average content, together with iron of terrigenous origin, is only 1%. These examples do not apply as support of the hypothesis favoring a volcanic source for the formation of the Gunflint facies. There could be, however, some supply of iron and silica derived from hot springs, but its amount was rather insignificant, if at all present. Speaking of cyclical sedimentation it seems at best conjectural that the banding of the formation was induced by the cyclical volcanic activities, especially if the regular Precambrian banded iron ores consisting at least of many hundred thousands bands are considered as the deep sea counterpart of the Gunflint formation. There seems to be no reason for considering the Gunflint ferruginous formation separately from other Precambrian banded iron ores. The presence of pyroclastics and lava along certain horizons seems not necessarily to imply a relationship between the iron formation and volcanism. The interbedding of volcanics with sedimentary rocks, without any consanguinity, is a regular feature of numerous stratigraphic sequences.

Goodwin suggests further that the submarine discharges of ferrous iron would not oxidize in the dominantly acid environment envisaged for the Gunflint basin. This assumption raises a question: Why is it necessary to resort to such unnatural conditions when it is known that sea water is non-acidic?

At least it seems probable that the acidity of such a large basin was due to the concentration of volcanic emanations in sea water. How could it be then explained the presence of siderite in the Gunflint formation?

If the volcanic emanations really were the main source of Gunflint formation and of the banded iron ores in general, minor elements characteristic for hot springs and fumaroles would be present (3, 7, 10, and 12). This would especially apply to the loci of volcanic activity described by Goodwin in the McTavish Township (p. 585) and possibly representing passageways of forceful liquid upsurge in connection with submarine springs. Lindgren (6) says that hot or cold springs (p. 68–69) may deposit limonite with As, Mn, and that carbonate and silica sinter of hot springs contain small quantities of Au, Cu, Pb, Zn, Sb, and Hg. The presence of these elements, if established, would support the point of view of the protagonists of a volcanic source for the formation of the Precambrian ferruginous deposits. But so far, no such evidence is available.

The principal objection to weathering as the source of iron and silica, according to Goodwin is the absence of Gunflint type iron formation from all rocks younger than Precambrian in age. The Gunflint formation probably had the same source as the Precambrian banded iron ores elsewhere. The deposition of the Gunflint formation was evidently favored by specific climatic conditions which were repeated during Precambrian time in different parts of the world. Periods during which the banded iron ores have been formed were separated by eras of about 600×10^6 to 750×10^6 years. The whole post-Precambrian time span embraces only 465×10^6 to 545×10^6 years and was evidently too short for the creation of conditions favorable for the deposition of banded ores similar to the Precambrian. This process requires selective weathering and transportation to the sea of iron hydroxide protected by organic matter during the cool season of the year and predominantly silica during the warm season (1). Regular banded iron ores evidently formed only under conditions of absolute exclusion of clastics.

Credit should be given to Goodwin for his suggestion that the atmosphere of the Gunflint time was oxidizing, because all shallow water facies contain ferric iron. This is another evidence that the Precambrian ferruginous formations were deposited under conditions which basically did not differ from those of the later geological periods. The creation of life contributed enormously to the possibility of migration of iron for long distances from the source on land. The first organisms probably appeared on land under conditions of orthoalluvium. Lithosphere, hydrosphere, and atmosphere, taken separately were unable to furnish an assemblage of organogenic elements necessary for the creation of life (9). This assemblage could be associated only at the surface of the lithosphere, moistened with water, and in presence of atmosphere. The first living organisms were protophores and had the capacity of active participation in destruction of rocks.

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February 28, 1957

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ABBREVIATIONS IN FIELD AND MINE GEOLOGICAL MAPPING

Sir: Mr. F. M. Chace's article, Abbreviations in Field and Mine Geological Mapping, which appeared in the November 1956 issue of Economic Geology, represents a great deal of work and provides a big step toward the adoption of a set of standard abbreviations. However, since the author has requested discussion, several inconsistencies should be pointed out.

In several instances Mr. Chace has failed to follow the rules that he proposed. His rule number 4 states, "Use of the same abbreviation for more than one word, obviously, should be avoided." On page 715 "ap" is the abbreviation for "aplite," but on page 716 "ap" is the abbreviation for "apatite." On page 717 "mag" means "magnetite" and on page 721 the same abbreviation means "magnetic." There are at least eight others.

There are also cases where Mr. Chace has used different abbreviations for the same word. On page 719 "medium" becomes "md," while on page 721 it is "med." On page 720, column 1, "cleavage" is abbreviated to "clvg" but in column 2 on the same page it is "cleav" where used in the term "fracture cleavage." On page 721 "very" is "vy," and on pages 719 and 720 "fine" is "fn," but on page 719 "very fine" is "vf," not "vy fn." There are many others.

These examples prompt me to suggest additional rules that might help to avoid such discrepancies. They are:

1. Use only one abbreviation for each word. (No explanation needed.)
2. When abbreviating two or more words, abbreviate each word separately, leaving a space between abbreviations.

By use of the second rule, "very coarse grained" would become "vy cse grnd" rather than "vcsg" which Mr. Chace suggests. This would eliminate the geologist's having to know that in some cases "very" is abbreviated as "vy"

and in others as "v," and that "course" can become either "cse" or "cs," and "grained" is abbreviated to "grnd" if it is used by itself (if that is possible) but to "g" when a qualifying term precedes it.

Several other criticisms that follow are minor. Among the list of Mineral and Metal Abbreviations are the terms "Gossan," "Laterite," "Oxide," "Sulfide" and "*Vein* quartz." Are these minerals or metals? Should they not be included in a more general list?

Some time ago a committee of the National Research Council prepared the Rock Color Chart, which among other things was intended to eliminate ambiguous terms such as "buff," "chocolate," "drab," "steel" and others. These terms should not be perpetuated by proposing abbreviations for them as was done on page 719.

Mr. Chace made what I consider to be a very worthwhile suggestion, then used it only occasionally. He wrote, "An acceptable abbreviation for certain minerals and rocks is obtained by leaving off the suffix 'ite.' . . ." Perhaps it would be feasible to strengthen this suggestion and make it into a rule with this connotation: When the result is not too awkward, abbreviate a rock or mineral name by dropping the suffix "ite." This rule would eliminate many ambiguous abbreviations; for example "la" is the suggested abbreviation for "latite." A person reading through his (or someone elses) notes could imagine "la" to stand for lava, labradorite, lapilli, laccolith, lamination, laterite —or any word beginning with "la." Of course this is an exaggeration, since the context would give a clue, but "lat" is far more suggestive of "latite" than is "la."

I hope that these suggestions will be helpful to Mr. Chace if he continues the task of compiling a list of abbreviations for universal adoption.

FRANK H. HOWD

EUREKA, UTAH,
Jan. 17, 1957

PROFESSIONAL ETHICS

Sir: In the September–October 1956 issue of your JOURNAL, there are two communications on the subject of professional ethics which are not only opportune in America but in Africa as well.

When I first studied mining engineering and geology, my professors took many opportunities of acquainting students with correct professional attitude and conduct. In the 1930's South African universities were small and probably it was very much simpler for the head of the department to inculcate good professional conduct than it is today. Nevertheless, most schools of geology in South Africa are not so large that this practice cannot be continued, but in fact less is done today than before, and the type of student coming to the university is not of the same high standard that obtained during the depression years.

With the present intense search for minerals all over Africa, field parties are being left alone a great deal, and with the long distances from drilling operations to the laboratory, the possibility of accidental or deliberate contamination, for example, becomes very great. In arduous climates the temp-

tation to cover the ground rapidly but not systematically also becomes great. Such conditions call for great loyalty to engaging parties, intense interest in the work for itself, and personal honesty. In field geophysical work I have seen many travesties of honesty because it was too hard to do the job the honest way.

Should professional geologists accept part payment in shares of the company that engages them or allied companies? Should professional geologists play the stock exchange? These points are important in the life of a young geologist.

I think that it is good for young geologists to move from one organization to another, and their knowledge from the one to the other is to the ultimate benefit of all. Knowledge is the professional geologist's capital, and it is important to know what amount of knowledge gained from one company can be used for another. Here, it is quite easy to define the limits of the knowledge that can be commonly used—namely so long as principles only are divulged, and not details that can identify a particular project either beneficially or otherwise, they can be used openly. It is impossible to open and close one's mind on each investigation and keep that knowledge locked up, nor is it in the interests of the parties concerned. Reputation is built upon experience developing from one investigation to another. Here guidance can be obtained from the medical and legal professional codes.

Young geologists leaving the university often have many openings available for them. It is their right to select the most advantageous in their opinion, but once having made that decision it is only fair to all that they should give at least a year's service to that company. I have been told of students who have had up to 12 posts in less than three years, and I have had geologists on my staff who have changed every three or four months. Such an attitude shows a lack of loyalty and perseverance, yet it is quite a commonplace one.

Many geologists employed by companies feel that having made a discovery, they are entitled to a special bonus, forgetting that for much of the time they have found nothing, and there have been no deductions because of that. Others frankly are willing to sell their information in the highest market.

I place part of the blame for much of the unethical conduct of young geologists on the academic staff. For example, I have known some graduates, not alone from one university, who feel that all geologic knowledge has been found by their professors or instructors, and names such as that of Lindgren, Daly, Niggli, Harker and for South Africans in particular du Toit, Wagner, Hall, Rogers and many others have no meaning. This is what Charles Park correctly calls plagiarism. I realize that in these days of extensive knowledge that during lectures, data must increasingly replace the details of how this knowledge was gained, but surely students must know the source of such knowledge if only to consult it in more detail? How often have I been told that the rock classification I use is one that was worked out by my professor or instructor, when in fact it is usually simply a modification of well known works?

A bad example is often set by organizations that should know better. For example, how often are papers published in which the field work has been done by a team or several teams and only a general acknowledgment made,

or even none at all? Yet scientific work is very much like a check, it is only as good as the signature. Full acknowledgment should always be made whether it is in a publication or a confidential report, for often at a later date a particular point may need amplification and if it is correctly indicated in the report then it is much easier to consult the person responsible for that section of the work.

The honesty of purpose of stating when a task is not within one's province is perhaps violated generally. It is perhaps not a very serious one, if every effort is made to solve the problem, but I have known consultants to take on an investigation without having the staff capable of carrying out the investigation, hoping that a long detailed report will hide the deficiencies.

I feel that the academic staff can and should do far more to raise the conduct of young geologists in South Africa, and apparently it is much the same in other countries.

V. L. Bosazza

Johannesburg, S. Africa,
Dec. 12, 1956

STABILITY RELATIONS OF SOME MINERALS IN THE Na_2O—Al_2O_3—SiO_2—H_2O SYSTEM

L. B. SAND, RUSTUM ROY, AND E. F. OSBORN

In the above paper which appeared on pages 169–179 (Vol. 52, No. 2) the authors inadvertently omitted the following table.

TABLE 1

X-Ray Data (Cr Unfiltered Radiation)
Nepheline Hydrate I

dÅ	Rel. I	dÅ	Rel. I
12.3	W	2.62	M
11.1	W	2.45	M
8.9	vW	2.30	W
8.1	S	2.21	W
7.4	S	2.12	W
6.3	M	2.05	W
5.9	vW	1.98	W
5.5	vW	1.89	W
5.2	vW	1.84	vW
5.0	M	1.75	W
4.7	M	1.72	W
4.38	vS		
4.21	vW	1.62	W
4.01	vW	1.56	vW
3.96	vW	1.51	W
3.73	M	1.473	vW
3.41	vS	1.385	vW
3.26	M	1.362	M
3.21	W	1.304	M
3.14	vW	1.287	M
2.97	S	1.278	W
2.87	M	1.247	vW
2.79	vW	1.222	vW
2.70	W		

vS = very strong; S = Strong; M = Medium; W = Weak; vW = very weak.

REVIEWS

Radiometriya [Radiometry]. By V. I. BARANOV. Pp. 343. Academy of Sciences, Moscow. 2nd (revised) edition, 1956. Price, 20r. 60k. (about $2.50). [Russian only.]

This interesting volume, compiled at the Vernadsky Institute for Geochemistry, reviews the various methods employed throughout the U.S.S.R. in laboratory and field measurements of radioactive minerals and ore deposits. Following some excellent theoretical chapters on the measurement of natural radioactivity, the book goes on to discuss somewhat inadequately problems of radioactivity in relation to geology; and then spends 200 pages on the description of equipment and methods employed in laboratory radiometric assay and in radiometric surveying in the field. Comparison with western practice reveals some interesting differences. Exploration for radioactive deposits by emanation methods, initially evolved in Russia in connection with oil prospecting, receives considerable attention; but scintillometric equipment is scarcely mentioned, whilst the use of radiometry in mining operations as in bore-hole logging and in stope control, is given but scant notice. A comparable work in English, but one giving greater attention to the practical problems of field work, would meet a present need.

C. F. DAVIDSON

Géologie et Géographie du Katanga. By MAURICE ROBERT. Pp. xv+620; pl. 67; figs. 74; colored maps, 7. Marcel Hayez, Brussels, 1956. Price, 1200 francs belges.

This large and thick volume is as comprehensive as its size and is given additional weight by the distinction of its author.

The monograph is divided into 3 parts. Part I is a study of the environment, and is made up of 4 chapters with subsections. Chapter I has a long section on stratigraphy and another one on tectonics and mineralization of Katanga. The subsection of mineralization treats of the copper, tin, uranium, gold, lead-zinc, platinum metals and iron. Chapter II is concerned with the climate of Katanga, and Chapter III is a systematic treatment of the relief and hydrology, taken up by areas. Chapter IV is Bibliography.

Part II is an interesting presentation of European penetration, discoveries, and native peoples and their migrations. This is given in 4 chapters.

Part III deals with the resources at length, divided into three chief sections, first the mineral resources; second, the agricultural, forest and fishery resources; and third, the energy resources and communications.

Under mineral resources the author takes up in Chapter I the development of beneficiation and metallurgy, which meant so much to the economic development of Katanga; in Chapter II, the exploitation of the mines of the Union Minière du Haut-Katanga. Chapter III deals with the history, production, reserves, treatment prices, and exportation of copper, cobalt, tin, gold, uranium, zinc, cadmium, germanium, silver, manganese, tungsten, tantalum and lithium minerals. There is practically no geology of the mineral deposits and very little about uranium.

The volume is full of information about Katanga and assembles in one reference all that is known about the stratigraphy and structural geology, and the geography. The work was published under the auspices of the Union Minière du Haut-Katanga in the celebration of the 50th year of its foundation.

The Barker Index of Crystals. By M. W. PORTER and R. C. SPILLER. Vol. II, Parts I, II, and III. W. Heffer & Sons Ltd., Cambridge, 1956. Price, £10.

Volume II of this compendium is devoted to the monoclinic system in three separate books. Part I is composed of Introduction and tables. Part II is Crystal Descriptions M.1 to M.1800. Part III is a continuation of M.1800 to M.3572. Part I has 58 pages of introductory matter and 325 pages of tables, including alphabetical lists of English chemical and mineralogical names, and one of German names as used by Groth, and a list of the compounds described in Parts II and III.

This second volume brings the number of chemical substances that can be identified from their crystal form to over 6,500. The three parts are devoted to crystals of the monoclinic system, into which fall over half the crystals whose measurements are known. The compendium constitutes an authoritative source for many compounds for which X-ray data are not available. The books are printed by offset from typed pages. The first book is paginated but the other two larger volumes are not paginated. An accompanying pamphlet gives directions for the use of the Barker Index. Workers in this field will need to have the Barker Index.

Clays and Clay Minerals—Fourth National Conference. Edited by ADA SWINEFORD. Pp. 444. Pub. No. 46, National Academy Sciences—National Research Council. Washington, D. C. 1956. Price, $6.00.

The Fourth National Conference on Clays and Clay Minerals was held at Pennsylvania State University in October, 1955, sponsored by the National Academy of Sciences—National Research Council, National Science Foundation and Pennsylvania State University. This volume contains 47 papers from three symposia that considered thermal transformations, clay-water relations, and mixed layer clays. The fields of the contributors include ceramics, geophysics, mineralogy, biology, soil chemistry, colloidal chemistry and physics.

The topics considered are mineral investigations in Spain, Belgium, Germany, Australia, and Japan; synthesis of clay minerals at low temperature; mechanism of dehydration of Mg-vermiculite; crystal structure of layer-lattice minerals; hydrogen-deuterium exchanges; kinetic study of montmorillonites by acid dissolution, weathering of clay minerals; techniques for X-ray diffraction analysis, and others.

This volume, like its predecessors of 1955 and 1956, brings together much new information on the rapidly growing field of clay minerals.

Coal Science, Aspects of Coal Constitution. By D. W. VAN KREVELEN and J. SCHUYER. Pp. 352; illustrated. Elsevier Publishing Co., Amsterdam, 1957. Price, $9.50.

The knowledge of the constitution of coal has been advancing by leaps and bounds in recent years. Most of the newer information, however, has been appearing in scientific journals. An up-to-date book in which this newer knowledge is assembled between two covers is more than welcome. It emanates from Holland by two Dutch specialists—one, Professor of Fuel Technology at Delft and Director of Research at the Central Laboratory, Netherland State Mines, and the other Re-

search Chemist at the same institution. Much of the information contained in the book is based upon the work carried on in their own laboratory.

The authors have divided the book into three parts. Part I takes up the technology, geology, petrology, chemistry, and physics of coal. Part II gives an account of statistical constitution analysis and its results and discusses the present structural picture. Part III deals with the other principal physical and chemical properties and offers interpretation of these properties by means of the structural picture. Each chapter carries extensive references, and each part is concluded with a "retrospect" in which the preceding subject matter is critically reviewed. The book is well illustrated by many graphs, charts, and photographs of coal constituents.

This is the first book in English covering the up-to-date treatment of the problems of the constitution and properties of coal and should prove invaluable to coal technologists everywhere.

The Metalliferous Mining Region of South West England, Vol. I, Vol. II. By H. G. DINES. Pp. 795; figs. 39; maps. Her Majesty's Stationery Office, London, 1956.

These two volumes summarize the geological information gained during mining in Cornwall, Devon, and Somerset; and J. Phemister has contributed petrographical notes. Chapter 2 treats of the geology of the region, and Chapter 3, the economic minerals of which tin and copper are the chief ores. Lead, zinc, silver and arsenic have also contributed considerably. Lists of all the minerals of each district are given in 25 pages of tables. Chapters 4 and 5 give details of the mines in the 14 districts. The information has been assembled through the field work of the author and many members of the Geological Survey and universities and from other government and private reports. It is an exhaustive treatment of these old mines, many of which were quite famous in their time.

America's Natural Resources. Edited for the Natural Resources Council of America, by CHARLES H. CALLISON. Pp. 211. Ronald Press, New York, 1957. Price, $3.75.

Natural resources are becoming uppermost in everyone's mind. This book, therefore, is of timely interest and will provide the background for an informed approach to the subject. It consists of the contributions of 11 authors dealing in separate chapters with soil, water, grasslands, forests, wild life, fish, parks and wildernesses, land use principles, renewable resources and human populations, ecology, and natural resources policy. Each author has discussed the historical background and the importance of the resource to human life.

The book is meant for the average citizen and is clearly written in a manner for all to read.

Physics and Chemistry of the Earth. Vol. I. Edited by L. H. AHRENS, K. RANKAMA, and S. H. RUNCORN. Pp. 317; illust. McGraw-Hill Book Co., New York, 1956. Price, $8.00.

This useful book is made of eight parts and a name and subject index. These parts are I, The Origin of the Solar System by Sir Harold Spencer-Jones; II, Temperatures Within the Earth by J. Verhoogen; III, Radioactive Methods for Determining Geological Age by L. H. Ahrens; IV, Seismology and the Broad Structure of the Earth's Interior by K. E. Bullen; V, The Hydrodynamics of the Earth's Core by Raymond Hide; VI, Investigations Under Hydrothermal Condi-

tions by Rustum Roy and O. F. Tuttle; VII, The Geochemistry of the Halogens by Carl W. Correns; and VIII, Geochemistry in the U.S.S.R. (1948–1953) by S. I. Tomkieff. Each part is followed by an extensive bibliography.

As will be seen, the listed authors are all outstanding in their respective fields. The parts of most interest to economic geologists are the Investigations Under Hydrothermal Conditions, the Geochemistry of the Halogens, and Geochemistry in the U.S.S.R. The first of these three deals with equipment, results of study, phase equilibrium in many systems, liquidous studies, and a summary. The second one deals with cosmos and meteorites, magmatic rocks, post-magmatic processes weathering, coal and oil, sediments, and metamorphic rocks. Geochemistry in the U.S.S.R. is made up of 5 chapters, namely, 1, Geochemistry, Geospheres, Elements; 2, Minerals; 3, Mineral Deposits; 4, Igneous Rocks; 5, Sedimentary Rocks; 6, Natural Waters and Evaporites. Each chapter carries an extensive bibliography of Soviet literature, probably the most complete ones available for these subjects.

The volume brings together much valuable data relating to earth sciences and should prove to be a welcome reference to geologists, geochemists, geophysicists and oceanographers, as well as physicists and chemists.

BOOKS RECEIVED

JAMES M. ALLEN

Light, Vegetation and Chlorophyll. J. TERRIEN, G. TRUFFAUT and J. CARLES. Pp. 228. Price, $6.00. Philosophical Library, New York, 1957. *A useful exposition of the present-day knowledge of photosynthesis. Physical and chemical aspects of the process and their implications.*

The Casting of Steel, edited by W. C. NEWELL. Pp. 599. Price, $27.50. Philosophical Library, New York, 1957. *Properties of liquid metal, melting and solidification, refractories, moulds, centrifugal casting, heat treatments, testing, radiography; 15 contributors. An authoritive book on all technical aspects of the production of steel castings.*

Scentific French. WILLIAM J. LOCKE. Pp. 112. Price, $2.50. John Wiley & Sons, New York, 1947. *A concise description of the structural elements of scientific and technical French; pronounciation, verbs, tenses, pronouns, adjectives, sentences.*

Scientific German. G. E. CONDOYANNIS. Pp. 163. Price, $2.50. John Wiley & Sons, New York, 1957. *The structural elements of scientific and technical German, giving pronounciation, structure, elements, noun-adjectives, word order, verbs, adjectives and adverbs; exercises in sentences.*

Uran, Die Metallischen Rohstoffe ihre Lagerungsverhältnisse und ihre wirtschaftliche Bedeutung. E. KOHL. Pp. 234, figs. 23. Ferdinand Enke, Stuttgart, 1954. *Occurrence, origin, host rocks, extraction, and occurrences in different countries; much out of date.*

Progress in Economic Geology. Edited by the Committee of the Commemorative Volume of Professor Takeo Kato, Takeo Watanabe, Chairman. Tokyo, 1956. *Thirty chapters by many authors divided into 5 parts dealing with 1) formation of ore deposits, 2) investigation of ores, 3) description of mines, 4) mining geology, and 5) scientific work of Professor Kato. All in Japanese except for English table of contents.*

Caves of Mssouri. J. HARLEN BRETZ. Pp. 490, figs. 168. Missouri Geological Survey and Water Resources, Rolla, Missouri, 1956. *Origin, patterns, topography, cave "formations," rate of growth, and detailed descriptions of caves.*

Laboratory Manual of Crystallography for Students of Mineralogy and Geology. GEORGE TUNELL and JOSEPH MURDOCK. Pp. 55, figs. 20. Price, $2.75. Wm. C. Brown Co., Dubuque, Iowa, 1957. *Architecture of crystals, measurement interfacial angles, classes of symmetry, use of crystallographic data in mineral identification.*

A Naturalist in Palestine. VICTOR HOWELLS. Pp. 180, pls. 29, figs. 13, map. Price, $6.00. Philosophical Library, New York, 1957. *Flora and fauna of Palestine and tales of the Arabs.*

Structural Outline of New Zealand. H. W. WELLMAN. Pp. 36, figs. 5. New Zealand Geological Survey, Department of Scientific and Industrial Research, Wellington, 1956. *A brief account of the structural geology of New Zealand.*

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Galactic Nebulae and Interstellar Matter. JEAN DUFAY. Pp. 352; pls. 24. Price, $15.00. *Atoms and molecules in space, solid particles in space, from atoms to grains and grains to stars, diffuse matter outside of the Milky Way. "The most complete account available of the many diverse phenomena, observational and theoretical, involved in the study of interstellar matter."*

Bibliography Geophysik. *100 cards—abstracts of papers, in German.*

Notice Explicative sur la Feuille Fort-Lamy. J. BARBEAU. Pp. 34, figs. 5, map. Gouvernement Général de l'Afrique Equatoriale Française, Paris, 1956. *Areal geology in the southwestern Sahara.*

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Memoirs of the Geological Survey of India, Volume 83. Petrology of Indian Coal. P. N. GANJU. Pp. 101, pls. 15. Price, 8s. *Occurrences, chemical characteristics, microscopic examination, summary.*

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Bulletin 7. Contribution à l'Etude Stratigraphique & Sedimentologique de la Basse-Kabylie (Region de Dellys-Tizi-Ouzou). PIERRE MURAOUR. Pp. 383, pls. 5, figs. 33. *Permian to recent formations of north central Algeria, geomorphology, paleontology, granodionite intrusive, geologic history.*

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Summary Report 39. Mineral Resources of Australia—Platinum Group Metals. Pp. 25, figs. 3, tbls. 8. Price, 3 sh. *Properties, industry, sources, production, consumption.*

Illinois Geological Survey—Urbana, 1957.

Circ. 225. Groundwater Geology in South-Central Illinois. L. F. SELKREGG, W. A. PRYOR and J. P. KEMPTON. Pp. 30, figs. 7.

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Geological Survey of India—Calcutta, 1954–56.

Volume 80. Review of the Mineral Production of India for the Years 1934–46 by the Director, and Senior Officers of the Geological Survey of India. Pp. 742, pl. 1. Price, 20s. 6d. *Review of mineral production 1934–46; occurrence, industry, reserves, and outlook.*

Volume 82, Part 4. M. S. KRISMAN and K. JACOB. Pp. 96, figs. 3, tbls. 15. Price, 5s. *Investigations of ilmenite, garnite and silica sands and slates.*

New Zealand Geological Survey—Wellington, 1955–56.

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Pennsylvania Geological Survey—Harrisburg, 1956.

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Circ. 8. The Mineral Industry of Pennsylvania in 1953. Alvin Kaufman. Pp. 26, tbls. 13.

Progress Rept. 149. Preliminary Report Geology and Mineral Resources of Southern Somerset County. Norman K. Flint. *Folio map and text giving general geolgy, coal, gas, and clay deposits.*

Progress Rept. 150. Oil and Gas Developments in Pennsylvania in 1955. C. R. Fettke and W. S. Lytle. Pp. 23, pls. 2, figs. 3, tbls. 4. *Includes well records and geology of new Greenlick gas pool.*

Bull. M38. Oil and Gas Geology of the Sheffield Quadrangle Pennsylvania. A. I. Ingham, W. S. Lytle, L. S. Matteson and R. E. Sherrill. Pp. 72, pls. 10, figs. 4, tbls. 3 *History, stratigraphy, structure, and origin of oil and gas sands.*

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University of Texas Bureau of Economic Geology—Austin, 1957.

Rept. of Investigaton 28. Upper Albian (Cretaceous) Ammonoidea from Texas. Keith Young. Pp. 33, pls. 10, figs. 4. *Classification; description of 12 new species.*

Rept. of Investigation 29. Ecological Interpretations of Pliocene and Pleistocene Stratigraphy in the Great Plains Region. J. C. Frye and A. B. Leonard. Pp. 11, figs. 3.

U. S. Geological Survey—Washington, D. C., 1957.

Prof. Paper 274-L. Volcanic Rocks of the El Modeno Area, Orange County, California. Robert F. Yerkes. Pp. 21, pls. 2, figs. 12, tbls. 4. Price, $1.00. *Petrographic and stratigraphic study of extrusive pyroclastic and flow rocks of middle to late Miocene age.*

Prof. Paper 289. Geology and Ore Deposits of the Garfield Quadrangle, Colorado. M. G. Dings and C. S. Robinson. Pp. 110, pls. 15, figs. 8. *Geology and description of replacement deposits and veins containing lead, silver, zinc and copper sulphides. Replacement deposits localized in dolomite and limestone, vein deposits chiefly in quartzite.*

Prof. Paper 291. Stratigraphy of the Uppermost Triassic and the Jurassic Rocks of the Navajo Country. J. W. Harshbarger, C. A. Repenning and J. H. Irwin. Pp. 74, pls. 3, figs. 38. *Stratigraphic study related to ground water resources.*

Bull. 1021-M. Ordovician Fossils from Wells in the Williston Basin, Eastern Montana. Reuben James Ross, Jr. Pp. 71, pls. 8, figs. 3, insert. Price, $1.00.

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Water-Supply Paper 1360-F. Salt Water and Its Relation to Fresh Ground Water in Harris County, Texas. A. G. WINSLOW, W. W. DOYEL, and L. A. WOOD. Pp. 32, pls. 4, figs. 11. *Extensive pumping caused larged cone of depression, which reversed hydraulic gradient with some influx of salt water.*

Water-Supply Paper 1360-G. Ground-Water Conditions in the Mendota-Huron Area, Fresno and Kings Counties, California. G. H. DAVIS and J. F. POLAND. Pp. 179, pls. 9, figs. 8, tbls. 3. *Details of an area where heavy pumping has made withdrawals greater than replenishment.*

Water-Supply Paper 1361. Geology and Ground-Water Resources of the York-James Peninsula, Virginia. D. J. CEDERSTROM. Pp. 237, pls. 9, figs. 21, tbls. 37. Price, $1.75.

SCIENTIFIC NOTES AND NEWS

Dr. ROBERT M. GARRELS, formerly associate professor of Geology at Harvard University, has been promoted to a full professorship.

SHELL COMPANIES FOUNDATION, INC., has announced that its contributions to educational, charitable, religious and public service organizations will top the million dollar mark for the third straight year. The amount, one of the largest in in industry, is allocated from gifts made to the Foundation by the several Shell companies, and more than $500,000 will go toward educational programs. Shell will provide 52 graduate fellowships and 20 grants for fundamental research to 43 colleges and universities and 90 full summer-term fellowships for high school science and mathematics teachers.

SHELDON L. GLOVER retired in February after 40 years of professional geologic work with the Division of Mines and Geology, Olympia, Washington. He has been supervisor of the Division for the past 12 years, was supervisor of the Division of Mines and Mining from 1941 to 1945, and was assistant supervisor of the predecessor agency, the Division of Geology, from 1934 to 1941.

MARSHALL T. HUNTTING was appointed by Governor Albert D. Rosellini to the position of Supervisor of the Washington State Division of Mines and Geology. Mr. Huntting has been on the staff of the Division and its predecessor agency, the Division of Geology, as a geologist since 1941, and for the past two years as Assistant Supervisor.

THE GEOLOGICAL SOCIETY OF AMERICA and ASSOCIATED SOCIETIES will hold their Annual Meetings at Atlantic City, New Jersey, November 4–6, 1957.

The NINTH PACIFIC SCIENCE CONGRESS OF THE PACIFIC SCIENCE ASSOCIATION will be in Thailand at Chulalongkorn University, Bangkok, November 18 to December 9, 1957.

The GULF COAST ASSOCIATION OF GEOLOGICAL SOCIETIES will hold its 7th Annual Convention November 6–8, 1957, at the Roosevelt Hotel, New Orleans, Louisiana.

The SIXTH NATIONAL CLAY CONFERENCE will be held at the University of California, in Berkeley, August 19–23. The program will include a field trip to major clay deposits in the area. Two full sessions will be devoted to clay genesis, one to fundamental characteristics and behavior of clay-liquid systems and one to subjects of general interest. A number of panel discussions and question-and-answer periods are also scheduled. The planning committee are chairman JOSEPH A. PASK, University of California; QUINTEN AUNE, U. S. Bureau of Mines, San Francisco; ISAAC BARSHAD, Department of Soils and Plant Nutrition, U.C.; GEORGE CLEVELAND, State Division of Mines, Los Angeles; GEORGE L. GATES, Division of Petroleum Technology, U. S. Bureau of Mines, San Francisco; IRVING GOLDBERG, Institute of Transportation and Traffic Engineering, U.C.; FRED R. KELLEY, Department of Soils and Plant Nutrition, U.C.; ALEXANDER KLEIN, Division of Civil Engineering, U.C.; CHARLES MEYER, Department of Geology, U.C.; ADOLF PABST, Department of Geology, U.C.; J. SCHLOCKER, Engineering Geology Branch, U. S. Geological Survey, Menlo Park; WILBUR H. SOMERTON, Petroleum

Engineering, Division of Mineral Technology, U.C.; EDWIN W. TOOKER, Mineral Deposits Branch, U. S. Geological Survey, Menlo Park. The meeting is presented by the Committee on Clays and Clay Technology of the College of Engineering, University of California, in cooperation with the Clay Minerals Committee, National Academy of Sciences, National Research Council. Further information and application for enrollment may be obtained from the Department of Conferences and Special Activities, University of California Extension, Berkeley 4, Calif.

The AMERICAN INSTITUTE OF MINING, METALLURGICAL, AND PETROLEUM ENGINEERS (AIME) now conducts its activities through a reorganized structure. Previously known as the Mining, Metallurgical and Petroleum Branches of AIME, these units now are the Society of Mining Engineers of AIME, the Metallurgical Society of AIME and the Society of Petroleum Engineers of AIME. Though each has its own officers and administrative set up, the three constituent Societies remain under control of the AIME Board of Directors. The national President of AIME is GROVER J. HOLT, General Manager of The Cleveland-Cliffs Iron Co. The Secretary is ERNEST O. KIRKENDALL. Headquarters of AIME and the mining and metallurgical societies are in New York. The petroleum headquarters continue in Dallas.

ELMER A. JONES is the first President of the Society of Mining Engineers of AIME. The President of the Metallurgical Society of AIME is JOHN C. KINNEAR, JR., of McGill, Nev., General Manager, Nevada Mines Division, Kennecott Copper Corp. The first President of the Society of Petroleum Engineers of AIME is JOHN P. HAMMOND, Assistant General Superintendent of Amerada Petroleum Co., Tulsa.

VICTOR OPPENHEIM and GLENN O. BRISCOE, Consultants, Petroleum and Mineral Explorations, have opened offices at Mercantile Securities Building, Suite 1206, Dallas 1, Texas.

PHILIP D. WILSON, One William Street, New York 4, N. Y., announces the removal of his office uptown to 100 Park Avenue, 34th Floor, New York 17, New York. He has been elected a vice president of Callahan Zinc-Lead Company.

The Gold Medal of the Institution of Mining and Metallurgy, London, for 1956, has been awarded to RANDOLPHE WILLIAM DIAMOND in recognition of his distinguished services to the mineral industry in Canada.

ALLEN F. AGNEW has been appointed State Geologist and Director of the South Dakota Geological Survey, beginning July 1, 1957, to replace Dr. E. P. ROTHROCK, who has resigned. The offices of the Survey will remain at the University of South Dakota in Vermillion, where he will continue to teach advanced and graduate courses in geology, part-time.

LUNA B. LEOPOLD has been made chief hydraulic engineer for the Geological Survey, and RAYMOND L. NACE has been made assistant chief of the Survey's Water Resources Division.

The GEOLOGICAL SOCIETY OF AMERICA, COAL GROUP, will hold the technical sessions at the national meeting of G.S.A. in Atlantic City, November 4–6, 1957. Those who wish to present papers must submit abstracts of 250 words or less in quadruplicate using G.S.A. forms. These abstracts should be returned to Ralph J. Gray by July 1 for the deadline for the final program is July 15.

FRANK D. SPENCER of the U. S. Geological Survey, completed in May, a two-year assignment on the coal resources of the Philippine Islands for the International Cooperation Administration in collaboration with the Philippine Bureau of Mines.

After a two-week examination of the coal deposits of Laos he returns to the United States via Europe and will be stationed again at Denver with the Fuels Branch of the U. S. Geological Survey.

JOSEPH HARRINGTON of the U. S. Geological Survey will arrive in Manila in June to take over his new assignment as Chief, Mining Division, International Cooperative Administration, Manila.

DUNCAN MCCONNELL, formerly professor and chairman of the Department of Mineralogy, The Ohio State University, has accepted a special research fellowship of the U. S. Public Health Service and is now research professor in the College of Dentistry, Ohio State University.

The TWELFTH ANNUAL FIELD CONFERENCE of the WYOMING GEOLOGICAL ASSOCIATION will be held in the Southwestern Wind River Basin September 12–14, with headquarters in Lander, Wyoming. A symposium will be combined with short field trips to explore the theme: Factors affecting the migration and accumulation of oil. Reservation blanks and detailed information may be obtained by contacting MIKE S. JOHNSON, Box 2249, Casper, Wyoming.

J. D. BATEMAN, Vice President of Ventures Limited, has been elected Chairman of the Board of the Bolivex Corporation, a company jointly owned by Ventures Limited, Toronto, and the Vitro Mineral Corporation, New York, which was formed recently to expore the mineral resources of Bolivia.

E. B. ALLEN, Jr.M.C.I.M., has left his position with Beaucage Mines, Ltd., and joined the staff of the Ontario Research Foundation as a Research Fellow.

MELVILLE L. BROWN, Jr.M.C.I.M., has been appointed Mine Superintendent for Renabie Mines, Ltd. Formerly he was Chief Geologist for Aunor Gold Mines, Ltd.

W. N. INGHAM has resigned as Resident Geologist, Val d'Or District, for the Quebec Department of Mines, and has set up headquarters in Toronto as a Consulting Geologist.

NEIL CAMPBELL has been appointed to the newly created position of senior geologist, special projects, for The Consolidated Mining and Smelting Company of Canada Limited.

ROBERT F. PETTIT has been named to the newly created position of chief engineer of American Smelting & Refining Company's northwest mining department at Wallace, Idaho.

IRA B. JORALEMON, consulting mining engineer and geologist, has been elected to the board of directors of the Bunker Hill Co., filling the vacancy created by the retirement of STANLY A. EASTON, chairman.

CECIL H. SMITH of Salt Lake City and REN DEMARS of Brigham City, Utah, have joined the staff of Vitro Minerals Corp. in Riverton, Wyoming.

GENE K. EALY, previously supervisor of exploration for the Colamer Corporation, is the new director of engineering and geology for United Western Minerals Company, Santa Fe, New Mexico.

HATFIELD GOUDEY is geologist in charge of the newly established field exploration office in Reno, Nevada, for American Exploration & Mining Company of San Francisco.

A. W. DERBY has resigned his position as Chief Geologist for the Dominion Gulf Company to establish a practice as Consulting Geologist with headquarters in Toronto.

THE GOVERNMENT OF THE BRITISH SOLOMON ISLANDS PROTECTORATE announces that the island of Bellona has been reopened to prospecting from April 29th. Phosphate has been proved by the Geological Survey Department, but not in as great a quantity as had been hoped. Some samples taken during pitting operations are high grade, and would be suitable for the manufacture of superphosphates. Full information may be obtained from the Senior Geologist, Geological Survey Department, Honiara, British Solomon Islands Protectorate.

M. L. THOMPSON, currently Head of the Department of Geology at the University of Kansas, Lawrence, has accepted the position of Principal Geologist in the Geological Resources Section at the Illinois State Geological Survey, Urbana. Dr. Thompson assumed his new duties on July 1, 1957.

HUBERT RISSER, currently Assistant Professor in the Department of Mining and Metallurgical Engineering at the University of Kansas, Lawrence, has accepted the position of Mineral Economist in the Mineral Economics Section at the Illinois State Geological Survey, Urbana. Dr. Risser began his appointment on July 1, 1957.

HOWARD G. SCHOENIKE, Economic Geologist of Houston, Texas, has announced his resignation as Production Geologist for the Baroid Division of the National Lead Company in order to devote full time to domestic and foreign consultation as a mining geologist. His headquarters will be at 4039 Turnberry Circle, Houston, Texas.

FRED L. HUMPHREY has left Stanford University to go to Brazil where he will organize a School of Geology at the University of Bahia.

THE INTERNATIONAL UNION OF GEODESY AND GEOPHYSICS, XITH GENERAL ASSEMBLY, will meet in Toronto, Ontario, Canada, September 3–14, 1957, at the University of Toronto.

W. MAURICE EWING, Director of the Lamont Geological Observatory of Columbia University, Palisades, N. Y., received the honorary degree of doctor of science during the 89th annual commencement exercises of Lehigh University on June 10. Mr. Ewing was a former faculty member at Lehigh for a decade.

BAHNGRELL W. BROWN has been named acting head of the Department of Geology at Montana School of Mines, Butte. He holds the rank of assistant professor and teaches courses in petrology, economic geology and engineering geology. His appointment will enable Professor WALTER S. MARCH, JR., former head of the department, to devote more time to his obligations as Associate Director of the Montana Bureau of Mines and Geology. Professor March will continue to teach a course within the geology department.

ERNEST L. OHLE has been appointed Chief Geologist in charge of the Geology Department of the Copper Range Company and White Pine Copper Company.

THE NEW MEXICO GEOLOGICAL SOCIETY will hold its Eighth Annual Field Conference in the Durango-Silverton-Ouray area of southwestern Colorado, September 5, 6, and 7, 1957. Participants are limited to 150. Write: Mrs. Marion Burks, Box 652, Socorro, New Mexico.

EDWARD B. BURWELL, JR., formerly Chief Geologist, Corps of Engineers, U. S. Army, has assumed practice as Consulting Engineering Geologist at Upperville, Virginia.

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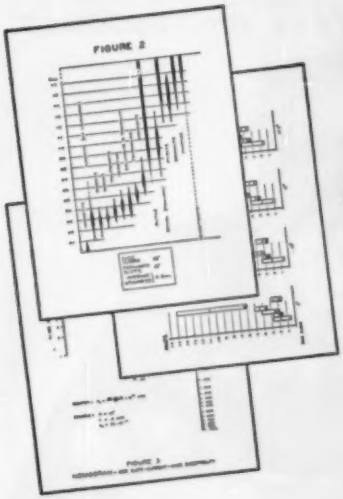

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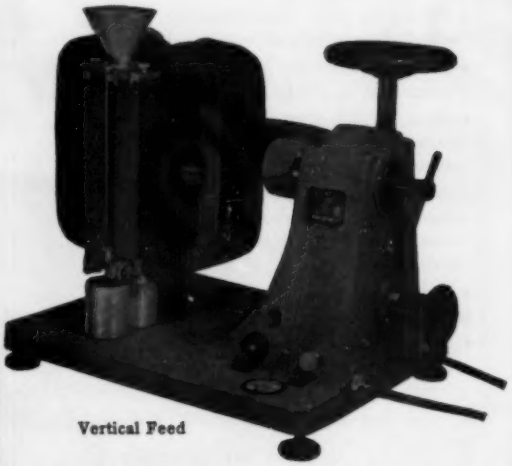

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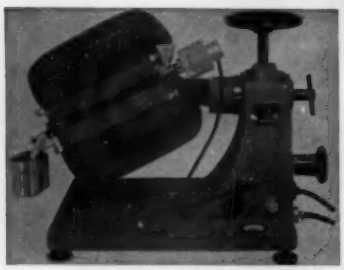

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